Second order susceptibility

The previous calculation can be generalized to higher-order terms in perturbation theory; in particular, one finds for the **second-order susceptibility**, in the limit of negligible absorption:

$$\chi^{(2)}_{\alpha\beta\gamma}(-\omega_\sigma : \omega_1, \omega_2) = \frac{N_p}{V\varepsilon_0 2\hbar^2}\mathcal{S}_\mathrm{T}\left\{\sum_{lmn}\rho^{(0)}_{ll}\left(\frac{\mu^{\alpha}_{ln}\,\mu^{\beta}_{nm}\,\mu^{\gamma}_{ml}}{(\Omega_{nl}-\omega_1-\omega_2)(\Omega_{ml}-\omega_2)}\right)\right\} \tag{4}$$

where the total symmetrization operator $\mathcal{S}_\mathrm{T}$ implies a summation over the six permutations of the pair $(\alpha, -\omega_\sigma)$, (β, ω_1), and (γ, ω_2), with $\omega_\sigma = \omega_1 + \omega_2$ as usual.

For the **third-order susceptibility** one arrives at

$$\chi^{(3)}_{\alpha\beta\gamma\delta}(-\omega_\sigma : \omega_1, \omega_2, \omega_3) = \frac{N_p}{V\varepsilon_0 3!\hbar^3}\mathcal{S}_\mathrm{T}$$
$$\left\{\sum_{nmlk}\rho^{(0)}_{nn}\left(\frac{\mu^{\alpha}_{nm}\,\mu^{\beta}_{ml}\,\mu^{\gamma}_{lk}\,\mu^{\delta}_{kn}}{(\Omega_{mn}-\omega_1-\omega_2-\omega_3)(\Omega_{ln}-\omega_2-\omega_3)(\Omega_{kn}-\omega_3)}\right)\right\}$$

Contracted notation

When the two excitation frequencies ω_1, ω_2 are far below resonance, or when they are close to each other, we can neglect dispersion in the $\chi^{(2)}$ tensor, meaning that it is invariant upon permutation of ω_1, ω_2 without touching the spatial indices:

$$\chi^{(2)}_{\underset{ijk}{\alpha\beta\gamma}}(-\omega_\sigma : \omega_1, \omega_2) = \chi^{(2)}_{\alpha\beta\gamma}(-\omega_\sigma : \omega_2, \omega_1) = \chi^{(2)}_{\alpha\gamma\beta}(-\omega_\sigma : \omega_1, \omega_2)$$

In the last equality, we used intrinsic permutation symmetry to show that $\chi^{(2)}$ remains invariant when the last two spatial indices are permuted. This reduces the number of independent elements from $3^3 = 27$ to $\underline{18}$, and the third-rank susceptibility tensor can be represented in a contracted form as a 3×6 matrix d_{il} with l taking values from 1 to 6 according to the correspondence:

l	1	2	3	4	5	6
jk	x	y	z	zy, yz	zx, xz	xy, yx

Conventionally, a factor 1/2 is also introduced, defining the tensor $\underline{\underline{d}} = \frac{1}{2}\underline{\underline{\chi}}^{(2)}$

d_{il} $\quad i = x, y, z \quad l = 1, 2, 3, 4, 5, 6$

Using this contracted notation, the second-order polarization vector writes

$$\begin{bmatrix} P_x^{(2)}(\omega_\sigma) \\ P_y^{(2)}(\omega_\sigma) \\ P_z^{(2)}(\omega_\sigma) \end{bmatrix} = 2\varepsilon_0 K(-\omega_\sigma : \omega_1, \omega_2)$$

$$\begin{array}{cc} & \quad\quad\quad 6 \\ 3 & \begin{bmatrix} d_{11} & \dots & d_{16} \\ d_{21} & \dots & d_{26} \\ d_{31} & \dots & d_{36} \end{bmatrix} \end{array} \cdot \begin{bmatrix} E_x(\omega_1)E_x(\omega_2) \\ E_y(\omega_1)E_y(\omega_2) \\ E_z(\omega_1)E_z(\omega_2) \\ E_y(\omega_1)E_z(\omega_2) + E_z(\omega_1)E_y(\omega_2) \\ E_x(\omega_1)E_z(\omega_2) + E_z(\omega_1)E_x(\omega_2) \\ E_x(\omega_1)E_y(\omega_2) + E_y(\omega_1)E_x(\omega_2) \end{bmatrix} \tag{5}$$

Under the stronger assumption of Kleinman symmetry (permutation of all 3 indices) the number of independent elements reduces to 10, as we have the following equalities:

$$d_{12} = d_{26} \quad ; \quad d_{13} = d_{35} \quad ; \quad d_{14} = d_{25} = d_{36} \quad ; \quad d_{15} = d_{31} \quad ; \quad d_{16} = d_{21}$$

$$d_{23} = d_{34} \quad ; \quad d_{24} = d_{32}$$

Effective nonlinear susceptibility $\chi^{(2)}_{\text{eff}}$ and d_{eff}

We consider two monochromatic fields at ω_1 and ω_2 whose amplitudes are $\boldsymbol{E}(\omega_j) = E_j \boldsymbol{e}_j$ where E_j is a scalar amplitude and $\boldsymbol{e}_j$ is the unit polarization vector. For example, $\boldsymbol{e}_1 = \frac{1}{\sqrt{2}}(\boldsymbol{u}_x + i\boldsymbol{u}_y)$ corresponds to a circularly polarized beam at ω_1. Applying the matrix product of eq. (5), we can write a compact expression for the second-order polarization component projected on a unit vector $\boldsymbol{e}_\sigma$:

$\vec{E}_1 \parallel x$

$$P^{(2)}_\sigma = \boldsymbol{P}^{(2)}(\omega_\sigma) \cdot \boldsymbol{e}_\sigma = 2\varepsilon_0 K(-\omega_\sigma : \omega_1, \omega_2)\, d_{\text{eff}}\, E_1 E_2 \tag{6}$$

$\vec{E}_2 \parallel z$

where the effective d-coefficient is a scalar parameter defined by

$\vec{P}_\sigma \parallel z$

$\hookrightarrow d_{35}$

$$d_{\text{eff}} = \sum_{ijk} d_{i(jk)}(\boldsymbol{e}_\sigma \cdot \boldsymbol{u}_i)(\boldsymbol{e}_1 \cdot \boldsymbol{u}_j)(\boldsymbol{e}_2 \cdot \boldsymbol{u}_k) = \frac{1}{2}\chi^{(2)}_{\text{eff}}(-\omega_\sigma : \omega_1, \omega_2) \tag{7}$$

Using tensor notation this relation is compactly expressed as

$$\chi^{(2)}_{\text{eff}}(-\omega_\sigma : \omega_1, \omega_2) = \boldsymbol{e}_\sigma \cdot \boldsymbol{\chi}^{(2)}(-\omega_\sigma : \omega_1, \omega_2) : \boldsymbol{e}_1 \boldsymbol{e}_2 \tag{8}$$

In the notation above, it should be understood that d_{eff} and $\chi^{(2)}_{\text{eff}}$ are functions of the polarization directions $(\boldsymbol{e}_\sigma, \boldsymbol{e}_1, \boldsymbol{e}_2)$, which are typically defined by the phase matching condition and belong to $\{\boldsymbol{e}_o, \boldsymbol{e}_\theta\}$.

Spatial symmetries

Let R be an orthogonal matrix representing a proper ($\det R = 1$) or improper ($\det R = -1$) rotation of space. If we apply this rotation to a nonlinear crystal, it can be shown that the nonlinear susceptibility tensor transforms according to

$$\chi^{(2)'}_{ijk} = R_{i\alpha} R_{j\beta} R_{k\gamma}\, \chi^{(2)}_{\alpha\beta\gamma} \tag{9}$$

where the summation on α, β, γ is implicit. A fundamental postulate in physics, known as Neumann's principle, states that **all physical properties of a system (e.g., a crystal) remain invariant under any coordinate transformation that leaves the system unchanged**; i.e., the symmetry elements of any physical property must include the symmetry elements of the system's point group. Here, each tensor component is counted as a physical property.
The simplest example is when the inversion symmetry (improper rotation) belongs to the system's point group:

$$R = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = -\mathbb{1}_{3\times 3}$$

Spatial symmetries

$$\chi^{(n)'}_{\ldots} = (-1)^{n+1} \chi^{(n)}_{\ldots}$$

Inserting R in eq. (9) leads to the equation

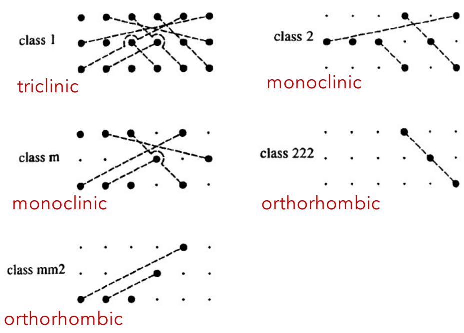
$$\chi^{(2)'}_{ijk} = (-1)^{\overset{2}{n}+1} \chi^{(2)}_{ijk}$$

Neumann's principle imposes $\chi^{(2)'}_{ijk} = \chi^{(2)}_{ijk}$, which implies that $\chi^{(2)} = \mathbf{0}$ for **all even values of** n, and in particular for $n = 2$.

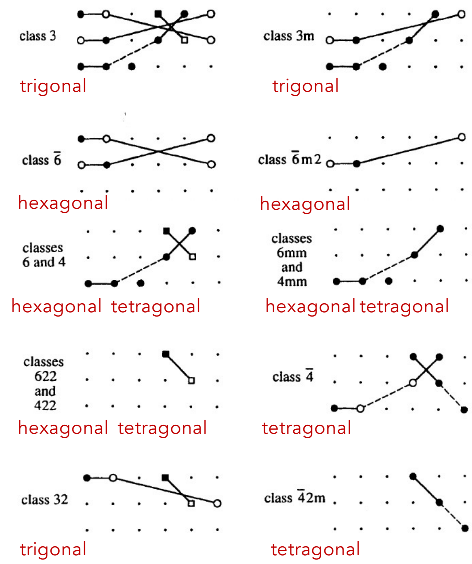
This method can be applied to all the symmetry elements of a given crystal's point group to reduce the number of independent components of the nonlinear susceptibility tensor (of any order), but it is a mathematically demanding procedure.

Spatial symmetries

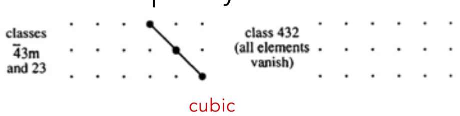
Biaxial crystal classes



Uniaxial crystal classes



Isotropic crystal classes



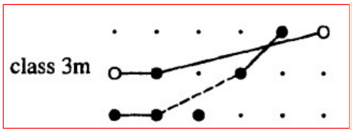
Class $\bar{4}2m$ $\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{bmatrix}$ $\{ d_{14} = d_{36}$

Solid line: equal elements
Open circle: opposite sign
Square: zero under Kleinman symmetry
Dashed line: equal under Kleinman symmetry

Butcher & Cotter Appendix 4 + Boyd Chapter 1

Common nonlinear crystals

Rhombohedral/trigonal (uniaxial)
Point group: 3m

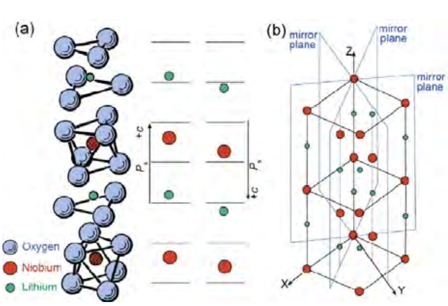


Solid line: equal elements
Open circle: opposite sign
Dashed line: equal under Kleinman symmetry

- Lithium niobate ($LiNbO_3$)

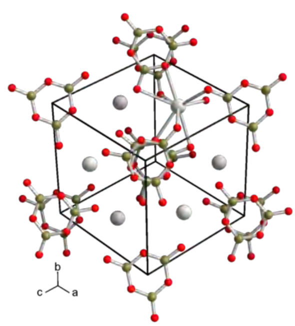
$$d_{33} \sim 20 - 40 \text{ pm/V}$$
$$d_{31} \sim 5 \text{ pm/V}$$
$$d_{22} \sim 2 - 3 \text{ pm/V}$$

https://www.tydexoptics.com/materials1/materials_for_nonlinear_optics/lithium_niobate/



- Barium borate (BBO)

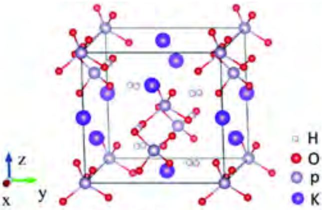
$$d_{31} < 0.1 \text{ pm/V}$$
$$d_{22} \sim 2 - 3 \text{ pm/V}$$

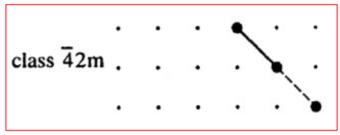


https://www.mt-berlin.com/frames_cryst/descriptions/bbo.htm

Common nonlinear crystals

Potassium dihydrogen phosphate (KDP)
- Tetragonal (uniaxial)
- Point group: -4 2 m

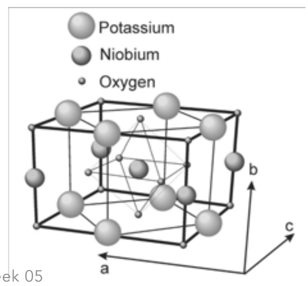


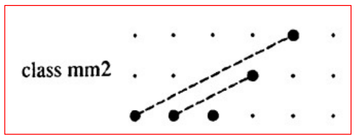


$$d_{36} \sim d_{14} = d_{25} \sim 0.3\ - 0.7\ \text{pm/V}$$

https://www.sciencedirect.com/topics/chemistry/second-order-nonlinear-optical-susceptibility

Potassium niobate ($KNbO_3$)
- Orthorhombic (biaxial)
- Point group: mm2





$$d_{31} \sim d_{15} \sim -16\ \text{pm/V}$$
$$d_{32} \sim d_{24} \sim -18\ \text{pm/V}$$
$$d_{33} \sim -28\ \text{pm/V}$$

History: second harmonic generation

VOLUME 7, NUMBER 4 PHYSICAL REVIEW LETTERS AUGUST 15, 1961

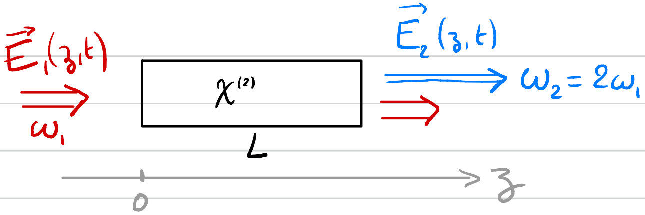
GENERATION OF OPTICAL HARMONICS*

P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich
The Harrison M. Randall Laboratory of Physics, The University of Michigan, Ann Arbor, Michigan
(Received July 21, 1961)

FIG. 1. A direct reproduction of the first plate in which there was an indication of second harmonic. The wavelength scale is in units of 100 A. The arrow at 3472 A indicates the small but dense image produced by the second harmonic. The image of the primary beam at 6943 A is very large due to halation.

Generation of Optical Harmonics
P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich
Phys. Rev. Lett. **7**, 118 – Published 15 August 1961

II) Second harmonic generation (SHG)



Undepleted pump:

$$\vec{E}_1(z,t) = \frac{1}{2}\Big(\underbrace{A_1 e^{ik_1 z}}_{E_{\omega_1}(z)} e^{-i\omega_1 t}\,\vec{e}_1 + c.c.\Big)$$

$$k_1 = \frac{\omega_1}{c} n(\omega_1)$$

$$\vec{P}^{(2)}_{2\omega_1}(z) = \varepsilon_0 \frac{1}{2} \underline{\underline{\chi}}^{(2)}(-2\omega_1 : \omega_1, \omega_1) : \vec{e}_1 \vec{e}_1 A_1^2 e^{i2k_1 z}$$

$$n_2 = n(2\omega_1)$$

We pose $\vec{E}_2(z,t) = \frac{1}{2}\Big(A_2(z)\, e^{ik_2 z}\, e^{-i\omega_2 t}\,\vec{e}_2 + c.c.\Big)$ with $\boxed{k_2 = \frac{2\omega_1}{c} n_2}$

Under the SVEA: $$\frac{dA_2}{dz} = \frac{i\omega_2}{2n_2\varepsilon_0 c} \vec{P}_{2\omega_1}(z)\cdot\vec{e}_2\, e^{-ik_2 z}$$

photon momentum..

$$2\hbar k_1 = \hbar k_2$$

where $$\vec{P}_{2\omega_1}(z)\cdot\vec{e}_2 = \varepsilon_0 \chi^{(2)}_{eff} A_1^2 e^{i2k_1 z}$$

so $$\boxed{\frac{dA_2}{dz} = \underbrace{\frac{i\omega_2}{2n_2 c}\chi^{(2)}_{eff} A_1^2}_{g}\; e^{i(2k_1 - k_2)z}}$$

Phase mismatch:

$$\Delta k = 2k_1 - k_2 = \frac{2\omega_1}{c}(n_1 - n_2)$$

Assume $A_2(z=0) = 0$

$$\sin(x) = \frac{e^{ix} - e^{-ix}}{2i}$$

$$A_2(z) = \int_0^z g\, e^{i\Delta k z'} dz' = \frac{g}{i\Delta k}\left(e^{i\Delta k z} - 1\right)$$

$$= g\, e^{i\frac{\Delta k}{2} z} \frac{\sin\left(\frac{\Delta k}{2} z\right)}{\frac{\Delta k}{2}} = \tilde{g}\; z \cdot \mathrm{sinc}\left(\frac{\Delta k}{2} z\right)$$

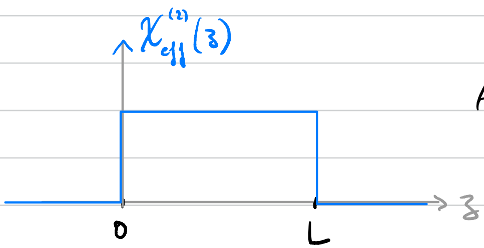
The SH intensity: $\boxed{I_2(z) \propto I_1\, \chi^{(2)}_{eff}\, z^2\, \mathrm{sinc}^2\left(\frac{\Delta k}{2} z\right)}$

* If $\Delta k = 0$: $I_2(z) \propto z^2$

* If $\Delta k \neq 0$: $I_2(z) \propto \sin^2\left(\frac{\Delta k}{2} z\right) \rightarrow$ oscillates

↳ first maximum when $\frac{\Delta k}{2} z = \frac{\pi}{2} \Leftrightarrow \boxed{z = \frac{\pi}{\Delta k} = L_c}$ "coherence length" of SHG

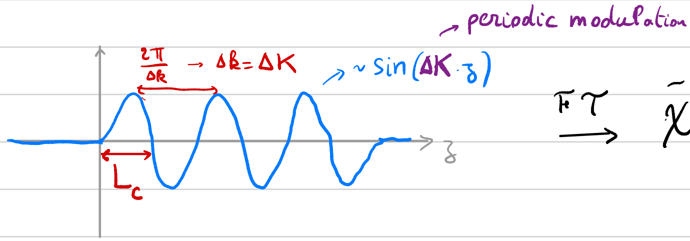
* Link with the Fourier Transform of $\chi^{(2)}_{eff}(z)$



$$A_2(z=L) \propto \int_{-\infty}^{+\infty} \chi^{(2)}_{eff}(z)\, e^{i \underbrace{\Delta k}_{\text{"k"}} z}\, dz = \tilde{\chi}^{(2)}_{eff}(k=\Delta k)$$

↓

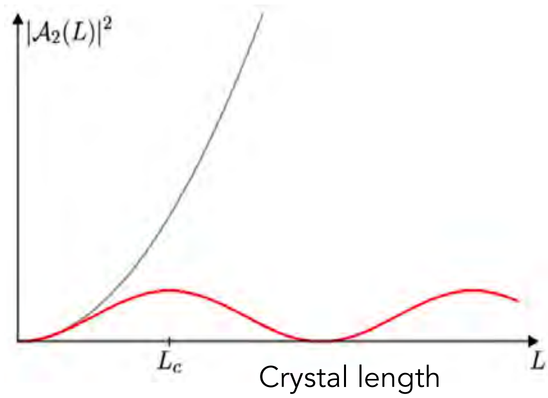
peaked at $\Delta k = 0$



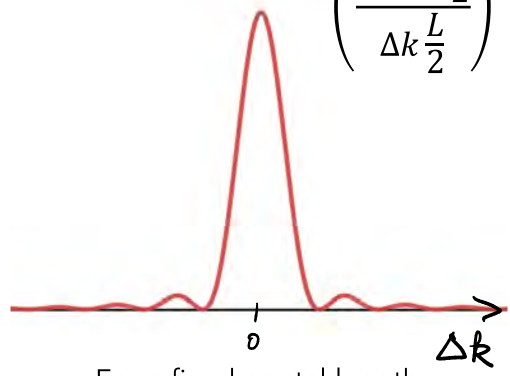
$$\xrightarrow{FT} \tilde{\chi}^{(2)}_{eff} \text{ peaked at } \pm \Delta K$$

Phase mismatch in SHG

SH intensity



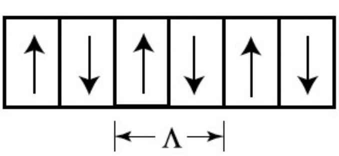
$$\left(\frac{\sin \Delta k \frac{L}{2}}{\Delta k \frac{L}{2}}\right)^2$$



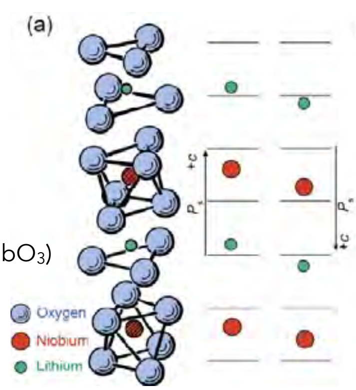
For a fixed crystal length

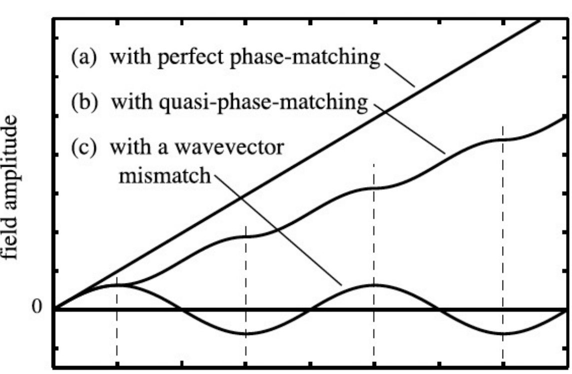
Quasi phase matching

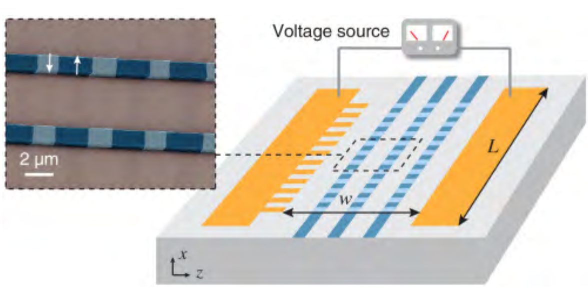
Periodically poled crystal:



Lithium niobate ($LiNbO_3$)







Ultrahigh-efficiency wavelength conversion in nanophotonic periodically poled lithium niobate waveguides
Cheng Wang et al. ***Optica*** Vol. 5, pp. 1438-1441 (2018)
https://doi.org/10.1364/OPTICA.5.001438

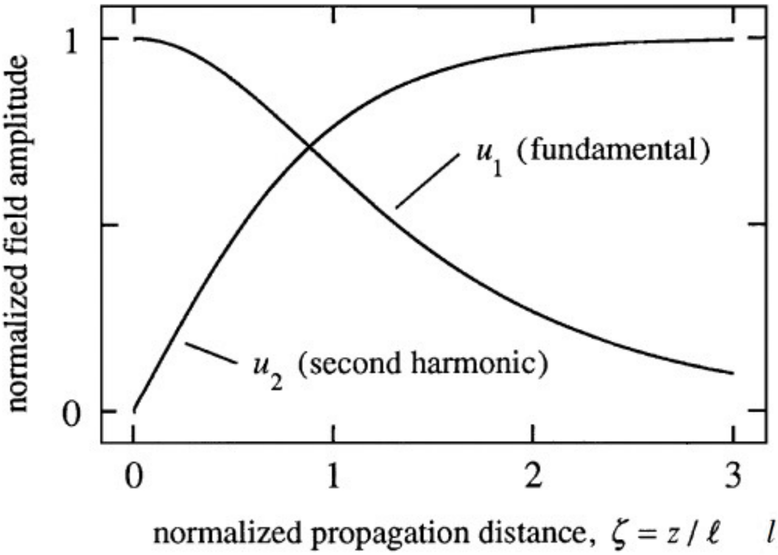
Source: Boyd Ch. 2.4

Effect of pump depletion

$\Delta k = 0$

$I_2(z) = I_1(0)\tanh^2(Gz)$

$I_1(z) = I_1(0)\,\mathrm{sech}^2(Gz)$



$$l = \frac{(n_1 n_2)^{1/2} c}{2\omega_1 d_{\mathrm{eff}} |A_1(0)|}$$

→ possible to convert into SHG

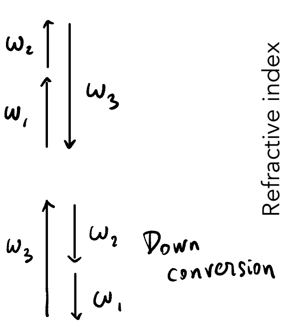
In practice $\geq 50\%$

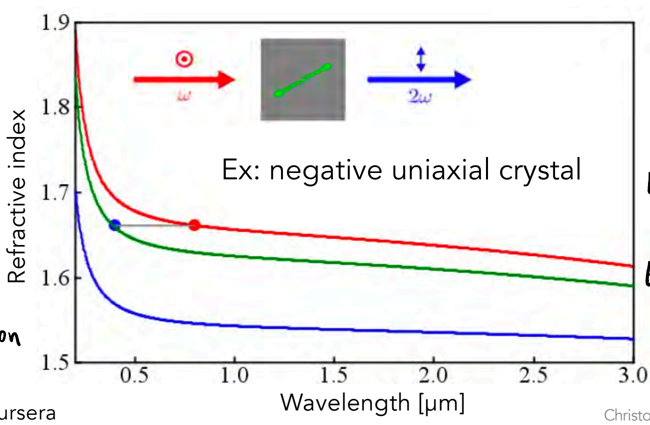
Source: Boyd Ch. 2.7

Phase matching types in three-wave mixing

- Type-I The two lowest-frequency beams have the same polarization
- Type-II The two lowest-frequency beams have orthogonal polarizations
- Type-0 All three waves have the same polarization

	Positive uniaxial ($n_e > n_0$)	Negative uniaxial ($n_e < n_0$)
Type I	$n_3^o\omega_3 = n_1^e\omega_1 + n_2^e\omega_2$	$n_3^e\omega_3 = n_1^o\omega_1 + n_2^o\omega_2$
Type II	$n_3^o\omega_3 = n_1^o\omega_1 + n_2^e\omega_2$	$n_3^e\omega_3 = n_1^e\omega_1 + n_2^o\omega_2$





For SPDC spontaneous parametric down conversion

type I = copolarized photon pairs

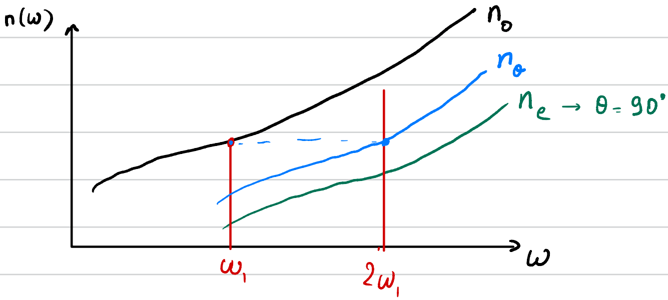
type II = cross polar.

Source: Manuel Joffre, Coursera

III) Phase matching using birefringence

1) Collinear

* Type I SHG in negative uniaxial crystal



$$n_o(\omega_1) = n_\theta(2\omega)$$