Generalized NL polarization

$$\mathbf{P}(\mathbf{r},t)=\sum_n\left[\mathbf{P}_n(r,t)\exp\left(i\left(\mathbf{k}_n\cdot\mathbf{r}-\omega_n t\right)\right)+c.c.\right]$$

- NL polarization does not necessarily point in the same direction as E field: must use tensors
- Second-order example: cartesion $\{i,j,k\}\in\{1,2,3\}$

$$P_i(\omega_n+\omega_m)=\varepsilon_0\sum_{jk}\sum_{(nm)}\chi^{(2)}_{ijk}(\omega_n+\omega_m;\omega_n,\omega_m)E_j(\omega_n)E_k(\omega_m)$$

- – Output i'th polarization direction, frequency $\omega_n+\omega_m$
- – Input polarization directions j, k, frequenies ω_n, ω_m
- – Sum (n m) so that $\omega_n+\omega_m$ is constant
- – Sum over + and – frequencies!

2nd order NL polarization example

- The susceptibility is a *tensor* **P** is in a different direction from **E**, each component of $\chi_{i\,j\,k}^{(2)}$ is a function
- Consider sum mixing to produce $\omega_3=\omega_1+\omega_2$ along the x-direction. The x component of the NL polarization is

$$P_1(\omega_3)=\varepsilon_0\sum_{jk}\begin{bmatrix}\chi^{(2)}_{1jk}(\omega_3;\omega_1,\omega_2)E_j(\omega_1)E_k(\omega_2)+\\ \chi^{(2)}_{1jk}(\omega_3;\omega_2,\omega_1)E_j(\omega_2)E_k(\omega_1)\end{bmatrix}$$

- – Permuting input frequencies
- – For a given set of input, output freq, $\chi_{1\,j\,k}^{(2)}$ is a 3x3 matrix

2^{nd} order NL polarization example

- All this looks hopelessly complicated, but typically…
  - We specify input frequencies and polarization
  - Phase matching allows us to focus on one output combination
  - Away from resonances, χ components indep of ω
- Examples: input $E_y(\omega_1)$ and $E_x(\omega_2)$

$$P_1(\omega_3) = \varepsilon_0\left[\chi_{121}^{(2)}E_2(\omega_1)E_1(\omega_2) + \chi_{112}^{(2)}E_1(\omega_2)E_2(\omega_1)\right]$$

- Input along y-direction $E_y(\omega_1)$ and $E_y(\omega_2)$

$$P_1(\omega_3) = 2\varepsilon_0\chi_{122}^{(2)}E_2(\omega_1)E_2(\omega_2)$$

- Because of crystal symmetry, many tensor components are either 0 or identical to others
- Negative frequency components go with conjugated fields

NL polarization: 2nd order

$$P_i^{(2)}(\omega_n+\omega_m) = \varepsilon_0\sum_{jk}\sum_{(nm)}\chi_{ijk}^{(2)}(\omega_n+\omega_m,\omega_n,\omega_m)E_j(\omega_n)E_k(\omega_m)$$

In this situation, each χ(2) is a 3x3 matrix, and the vector form would be written

$$P_i^{(2)}(\omega_n+\omega_m) = \varepsilon_0\sum_{(nm)}\mathbf{E}(\omega_n)\bullet\ddot{\chi}_i^{(2)}(\omega_n+\omega_m;\omega_n,\omega_m)\bullet\mathbf{E}(\omega_m)$$

In matrix form, this would be

$$P_1^{(2)}(\omega_3=\omega_1+\omega_2) = \varepsilon_0\begin{pmatrix} E_1(\omega_1) & E_2(\omega_1) & E_3(\omega_1)\end{pmatrix}\begin{pmatrix}\chi_{111} & \chi_{112} & \chi_{113}\\ \chi_{121} & \chi_{122} & \chi_{123}\\ \chi_{131} & \chi_{132} & \chi_{133}\end{pmatrix}\begin{pmatrix}E_1(\omega_2)\\ E_2(\omega_2)\\ E_3(\omega_2)\end{pmatrix}$$

$$+\varepsilon_0\begin{pmatrix} E_1(\omega_2) & E_2(\omega_2) & E_3(\omega_2)\end{pmatrix}\begin{pmatrix}\chi_{111} & \chi_{112} & \chi_{113}\\ \chi_{121} & \chi_{122} & \chi_{123}\\ \chi_{131} & \chi_{132} & \chi_{133}\end{pmatrix}\begin{pmatrix}E_1(\omega_1)\\ E_2(\omega_1)\\ E_3(\omega_1)\end{pmatrix}$$

We need to use as many symmetries as possible to reduce the complexity.
can reduce from ~ 324 terms to 10 or fewer

Centro-symmetric media

- For second-order response, the potential must have asymmetry.
- When the binding potential for the electrons is centrally symmetric, the response can still be nonlinear, but the order must be odd (3rd, 5th, etc).
- Consider a central restoring force:

$$\mathbf{F}(\mathbf{r}) = -m\omega_0^2\mathbf{r} + mb(\mathbf{r}\cdot\mathbf{r})\mathbf{r}$$

$$F_i(\mathbf{r}) = -m\omega_0^2 r_i + mbr_j r_j r_i$$

  - force is always directed along $\hat{\mathbf{r}}$ direction
  - At large r, force is less binding.
- As with the non-centrosymmetric potential, perform perturbation expansion.
  - $x^{(2)}$ does not contribute, so $\chi^{(2)}=0$

Solution of 3rd order

- Each term for 1st order solution can be a different frequency

$$\ddot{x}^{(3)} + 2\gamma\dot{x}^{(3)} + \omega_0^2 x^{(3)} = b\left(x^{(1)}\right)^3$$

$$\left(\ddot{x}^{(3)}(\omega_q) + 2\gamma\dot{x}^{(3)}(\omega_q) + \omega_0^2 x^{(3)}(\omega_q)\right)e^{-i\omega_q t} = b\sum_{mnp} x^{(1)}(\omega_m)x^{(1)}(\omega_n)x^{(1)}(\omega_p)e^{-i(\omega_m+\omega_n+\omega_p)t}$$

  - Note the m, n, p can all be + or – : for example, $\omega_{-2} = -\omega_2$
  - Enforce energy conservation, so

$$\omega_q = \omega_m + \omega_n + \omega_p \rightarrow (mnp) \quad \text{in summation}$$

- Solution is

$$\mathbf{r}^{(3)}(\omega_q) = -\sum_{(mnp)} \frac{be^3}{m^3} \frac{(\mathbf{E}(\omega_m)\cdot\mathbf{E}(\omega_n))\mathbf{E}(\omega_p)}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

$$\mathbf{P}^{(3)}(\omega_q) = -Ne\mathbf{r}^{(3)}(\omega_q) = +\sum_{(mnp)} N\frac{be^4}{m^3} \frac{(\mathbf{E}(\omega_m)\cdot\mathbf{E}(\omega_n))\mathbf{E}(\omega_p)}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

Calculation of χ$^{(3)}$

- 3rd order NL polarization is

$$\mathbf{P}^{(3)}(\omega_q) = \sum_{(mnp)} N \frac{be^4}{m^3} \frac{\left(\mathbf{E}(\omega_m)\cdot\mathbf{E}(\omega_n)\right)\mathbf{E}(\omega_p)}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

- Defined in terms of the susceptibility

$$P_i^{(3)}(\omega_q) \equiv \varepsilon_0 \sum_{jkl}\sum_{(mnp)} \chi_{ijkl}^{(3)}(\omega_q,\omega_m,\omega_n,\omega_p)E_j(\omega_m)E_k(\omega_n)E_l(\omega_p)$$

- χ$^{(3)}$ is a *tensor*:
  - *i j k l* are *coordinate* indices (1, 2, 3 or *x, y, z*) that correspond to the directions of the *field* polarizations: *i* is output, *j, k, l* are distinct inputs
  - q, m, n, p are frequency indices of the distinct fields
  - All indices can potentially be the same
  - (mnp) in summation means $\omega_q = \omega_m + \omega_n + \omega_p$

χ$^{(3)}$ tensor

- Convert vector P to summation: e.g.

$$\mathbf{E}(\omega_m)\cdot\mathbf{E}(\omega_n) = \sum_j E_j(\omega_m)E_j(\omega_n) = \sum_{jk} E_j(\omega_m)E_k(\omega_n)\delta_{jk}$$

- 3rd order NL susceptibility is

$$P_i^{(3)}(\omega_q) = \sum_{jkl}\sum_{(mnp)} N \frac{be^4}{m^3} \frac{E_j(\omega_m)E_k(\omega_n)E_l(\omega_p)\delta_{jk}\delta_{il}}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

$$P_i^{(3)}(\omega_q) \equiv \varepsilon_0 \sum_{jkl}\sum_{(mnp)} \chi_{ijkl}^{(3)}(\omega_q,\omega_m,\omega_n,\omega_p)E_j(\omega_m)E_k(\omega_n)E_l(\omega_p)$$

$$\chi_{ijkl}^{(3)}(\omega_q,\omega_m,\omega_n,\omega_p) = \frac{Nbe^4}{\varepsilon_0 m^3} \frac{\delta_{jk}\delta_{il}}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

- Account for "intrinsic permutation symmetry"
  - Fields $E_j(\omega_m)E_k(\omega_n)E_l(\omega_p)$ can be in any order

$$\chi_{ijkl}^{(3)}(\omega_q,\omega_m,\omega_n,\omega_p) = \frac{Nbe^4}{3\varepsilon_0 m^3} \frac{\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}}{D(\omega_q)D(\omega_m)D(\omega_n)D(\omega_p)}$$

  - 3 terms aren't there b/c of dot product of fields

Summary of intrinsic symmetries for NL tensor

- Real fields and polarization

$$E_j(-\omega_n) = E_j^*(\omega_n) \quad P_i(-\omega_m - \omega_n) = P_i^*(\omega_m + \omega_n)$$

$$P_i^{(2)}(\omega_n + \omega_m)^* = \varepsilon_0 \sum_{jk} \sum_{(nm)} \chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m)^* E_j(\omega_n)^* E_k(\omega_m)^*$$

$$P_i^{(2)}(-\omega_n - \omega_m) = \varepsilon_0 \sum_{jk} \sum_{(nm)} \chi_{ijk}^{(2)}(-\omega_n - \omega_m, -\omega_n, -\omega_m) E_j(-\omega_n) E_k(-\omega_m)$$

- Intrinsic permutation symmetry:
  - j, k and m, n are dummy indices

$$\chi_{ijk}^{(2)}(\omega_n + \omega_m, \omega_n, \omega_m) E_j(\omega_n) E_k(\omega_m) = \chi_{ikj}^{(2)}(\omega_n + \omega_m, \omega_m, \omega_n) E_k(\omega_m) E_j(\omega_n)$$

  - Swap j k and n m at same time. Not i and q in this case

Other common symmetries

- Lossless media (not always true)
  - Real components of $\chi^{(2)}$. Usually true if incident frequencies and their combinations are away from resonances.
  - full permutation symmetry: free interchange of all ω components, as long as i, j, k are swapped at same time.

- Kleinmans's symmetry (if dispersion of $\chi^{(2)}$ can be neglected)
  - Dispersion is intrinsically linked to time response. So if we neglect dispersion, it is the same as assuming NL response is instantaneous.
  - In this case, we can permute I j k without also permuting ω's
  - This makes χ tensors symmetric
- **Note:**
  - From practical perspective of using NL crystals, many desirable crystals are designed to be transparent, non-dispersive, etc.
  - But for characterizing materials, measuring NL response leads to important information about structure and internal energy levels

Spatial symmetries

- Crystal structure leads to spatial symmetries: 32 different crystal point groups.
- Example: 4-fold symmetry around z-axis means $\chi_{zxx}=\chi_{zyy}$
- Spatial symmetry affects
  - linear optical properties (birefringence, optical activity)
  - high-order χ tensors
  - Even if $\chi^{(1)}$ is isotropic, $\chi^{(3)}$ may not be. Ex: XPW generation
- Inversion symmetry and $\chi^{(2)}$

$$P(t)=\varepsilon_0\chi^{(2)}E^2(t)$$

  - If medium is centrosymmetric (possesses inversion symmetry), then P(t) must have same sign as E(t)

$$-P(t)=\varepsilon_0\chi^{(2)}\left(-E(t)\right)^2$$

  - This means that $\chi^{(2)}$ must vanish.

Contracted notation: non-dispersive, non-absorbing medium

Use one d-matrix instead of three

Non-dispersive: can permute any spatial index (Kleinmann symm)
- like colors have the same value, except black terms are unique

$$\begin{pmatrix} d_{xxx} & d_{xxy} & d_{xxz} \\ & d_{xyy} & d_{xyz} \\ & & d_{xzz} \end{pmatrix} \quad \begin{pmatrix} d_{xxy} & d_{xyy} & d_{xyz} \\ & d_{yyy} & d_{yyz} \\ & & d_{yzz} \end{pmatrix} \quad \begin{pmatrix} d_{xxz} & d_{xyz} & d_{xzz} \\ & d_{yyz} & d_{yzz} \\ & & d_{zzz} \end{pmatrix}$$

$$\rightarrow \begin{pmatrix} d_{xxx} & d_{xyy} & d_{xzz} & d_{xyz} & d_{xxz} & d_{xxy} \\ d_{xxy} & d_{yyy} & d_{yzz} & d_{yyz} & d_{xyz} & d_{xyy} \\ d_{xxz} & d_{yyz} & d_{zzz} & d_{yzz} & d_{xzz} & d_{xyz} \end{pmatrix}$$

$$\downarrow$$

$$\begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{zzz} & d_{23} & d_{13} & d_{14} \end{pmatrix}$$

Symmetry in d-matrices

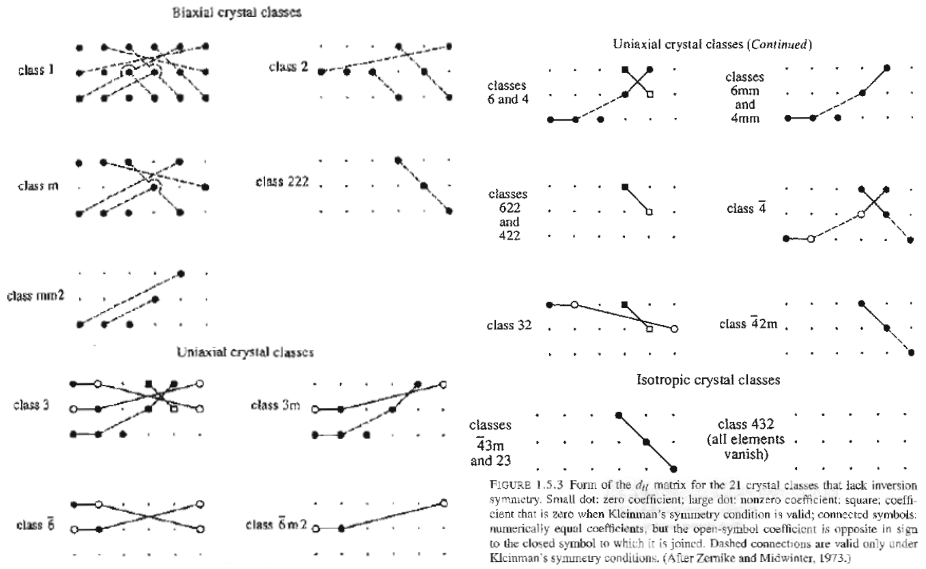


FIGURE 1.5.3 Form of the d_{il} matrix for the 21 crystal classes that lack inversion symmetry. Small dot: zero coefficient; large dot: nonzero coefficient; square: coefficient that is zero when Kleinman's symmetry condition is valid; connected symbols: numerically equal coefficients, but the open-symbol coefficient is opposite in sign to the closed symbol to which it is joined. Dashed connections are valid only under Kleinman's symmetry conditions. (After Zernike and Midwinter, 1973.)

Effective NL coefficient

- *d*-matrix contains NL tensor coefficients for each crystal type
- Orientation of crystal affects effective NL strength
- Example: BBO, 3m symmetry

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{31} & d_{22} \\ -d_{22} & d_{22} & 0 & d_{31} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} E_{1x}E_{2x} \\ E_{1y}E_{2y} \\ E_{1z}E_{2z} \\ E_{1z}E_{2y} + E_{1y}E_{2z} \\ E_{1z}E_{2x} + E_{1x}E_{2z} \\ E_{1y}E_{2x} + E_{1x}E_{2y} \end{pmatrix}$$

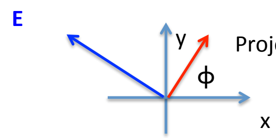
Example calculation of d_{eff}

- For type I phase matching:
  - **Input E$_1$** and **E$_2$** are polarized in the same direction
  - Both are o-waves, no projection on z-axis (optic axis), $\hat{\mathbf{D}} = \hat{\mathbf{E}}$
  - Define **s** (= unit vector for **k**) in spherical coords,

    $\mathbf{s} = \hat{\mathbf{k}} = \{\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta\}$
  - Find direction of **E** consistent with **k**:

$$\mathbf{E}\cdot\mathbf{s} = 0$$
$$E_1\cos\phi_E\sin\theta\cos\phi + E_1\sin\phi_E\sin\theta\sin\phi = 0$$
$$\cos\phi_E\cos\phi + \sin\phi_E\sin\phi = 0$$
$$\cos(\phi_E - \phi) = 0$$
$$\phi_E - \phi = \pi/2$$

$$E_1 = E_{10}\{-\sin\phi, \cos\phi, 0\}$$
$$E_2 = E_{20}\{-\sin\phi, \cos\phi, 0\}$$



Projection of **s** onto x-y

Induced polarization

- Compose the E$_1$E$_2$ vector:
- The d-matrix is used to calculate the induced NL polarization

$$\begin{pmatrix} E_{1x}E_{2x} \\ E_{1y}E_{2y} \\ E_{1z}E_{2z} \\ E_{1z}E_{2y}+E_{1y}E_{2z} \\ E_{1z}E_{2x}+E_{1x}E_{2z} \\ E_{1y}E_{2x}+E_{1x}E_{2y} \end{pmatrix} \Rightarrow \begin{pmatrix} E_1E_2\sin^2\phi \\ E_1E_2\cos^2\phi \\ 0 \\ 0 \\ 0 \\ -E_1E_2\sin\phi\cos\phi \end{pmatrix}$$

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & d_{31} & d_{22} \\ -d_{22} & d_{22} & 0 & d_{31} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} E_1E_2\sin^2\phi \\ E_1E_2\cos^2\phi \\ 0 \\ 0 \\ 0 \\ -E_1E_2\sin\phi\cos\phi \end{pmatrix} = \begin{pmatrix} d_{22}E_1E_2\sin 2\phi \\ d_{22}E_1E_2\cos 2\phi \\ d_{32}E_1E_2 \end{pmatrix}$$

D-matrix for BBO

SHG along all axes

Finding the e-wave (SH) vector

- Note that NL polarization is induced at 2ω in all 3 directions $\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} d_{22}E_1E_2\sin 2\phi \\ d_{22}E_1E_2\cos 2\phi \\ d_{32}E_1E_2 \end{pmatrix}$
- The generated e-wave unit vector **a** must be perpendicular to $\mathbf{E_1}$ and **s**

$$\mathbf{E_1}\cdot\mathbf{a} = 0 \rightarrow -E_{10}\sin\phi\, a_0\sin\theta_a\cos\phi_a + E_{10}\cos\phi\, a_0\sin\theta_a\sin\phi_a = 0$$
$$\sin\phi\cos\phi_a = \cos\phi\sin\phi_a \rightarrow \phi_a = \phi$$

$$\mathbf{a}\cdot\mathbf{s} = 0 \rightarrow a_0\cos\theta_a\cos\theta + a_0\sin\theta = 0$$
$$\cos\theta_a = -\tan\theta$$

- **a** is a unit vector, so from **a.a** = 1

$$a_0 = \cos\theta \qquad \rightarrow \mathbf{a} = \{\ \cos\theta\cos\phi \quad \cos\theta\sin\phi \quad -\sin\theta\ \}$$

Component of P that drives e-wave

- Pick out component that will drive a wave propagating in the direction of **k** (= **s**) and that is an e-wave

$$\mathbf{P}\cdot\mathbf{a} = d_{eff}E_1E_2 \rightarrow d_{eff} = d_{31}\sin\theta - d_{22}\cos\theta\sin 3\phi \qquad \text{(1.5.30a)}$$

- For type II,

$$d_{eff} = d_{22}\cos^2\theta\cos 3\phi \qquad \text{(1.5.30b)}$$

- Different relations for crystals with different symmetry
- These equations are used to optimize the orientation of the crystal for maximum signal
- Some directions that could be phase-matched don't have an induced polarization in the right direction

Common NL crystals

- KDP, KD*P:
  - uniaxial, can grow large crystals, low dispersion.
  - Doubling, OPA Pockels cells,…
- BBO:
  - uniaxial, high NL coeff good UV transmisson,
  - Doubling, OPA, Pockels cells…
- KTP:
  - biaxial, high NL coeff for typeII doubling
- LBO:
  - biaxial, high damage threshold
- $LiNbO_3$:
  - pockels cells, PPLN
- Newer: BiBO, ZGP
- Suppliers: Casix, Castech, EKSMA, Quantum Tech, Cleveland Crystals…

Evaluating crystals for applications

- Transparency for spectral region
- Orientations that allow for NL response (tensors), strength of NL coefficient
- Phase-matching geometries allowed
- Damage threshold (max intensity)
- Thermal issues (change in index with temperature)
- CW: birefringent walk-off (sets limit for crystal length)
- Angular acceptance: limits divergence of input, crystal length
- Short pulses: dispersion/phase matching bandwidth, connected to group velocity walkoff
- Dimensions of crystal, cost