Molecular Design Strategies for Optimizing the Nonlinear Optical Properties of Chiral Crystals

Ronald D. Wampler, Nathan J. Begue, and Garth J. Simpson*

ABSTRACT: A simple theoretical framework is presented to identify the key molecular properties and macromolecular arrangements leading to high second-order nonlinear optical (NLO) activity of chiral crystals. In chiral materials, maximum second harmonic generation (SHG) efficiency is predicted for an *antiparallel molecular arrangement of Λ-like chromophores.* This prediction is in stark contrast to the majority of previous crystal engineering efforts for second-order NLO materials, which have been focused almost exclusively on *the construction of crystals exhibiting high degrees of polar order*. Methods for possible rational electrostatic control of crystal structure by appropriate molecular design are considered.

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Introduction

Chiral crystals have the distinct advantage of necessarily **lacking inversion symmetry** and therefore always exhibiting **symmetry-allowed SHG.**

However, symmetry alone does not necessarily provide a direct indication of the efficiency of SHG-activity**, suggesting the need for a rational design framework**

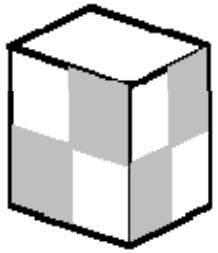
Theory

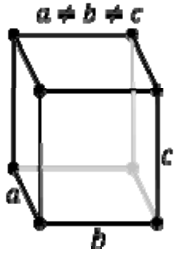
crystal structure of chiral molecules :

- noncentrosymmetric
- SHG-active

either

the Orthorhombic $P2_12_12_1$ space groups (~55%)



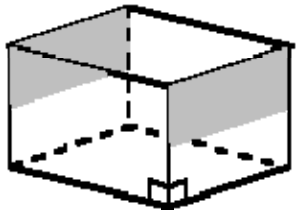


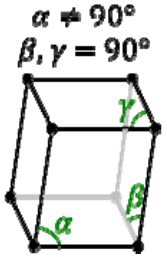
three unique tensor elements remain:

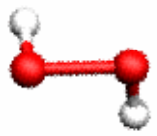
$\chi_{XYZ} = \chi_{XZY}$, $\chi_{YZX} = \chi_{YXZ}$, $\chi_{ZXY} = \chi_{ZYX}$

or

the Monoclinic $P2_1$ space groups (~34%)







H_2O_2(Hydrogen peroxide)

http://www.staff.ncl.ac.uk/j.p.goss/symmetry/

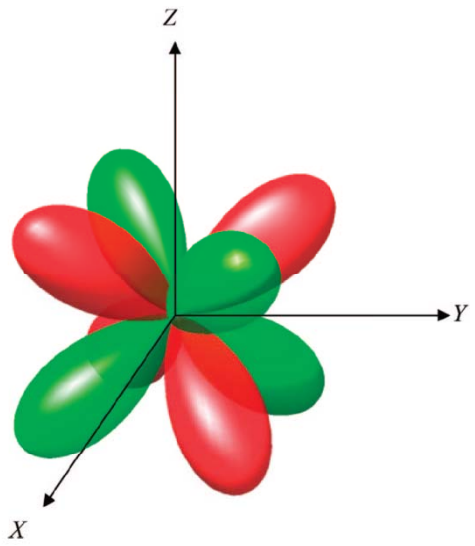
http://en.wikipedia.org/wiki/Space_group

http://ko.wikipedia.org/wiki/%EA%B3%B5%EA%B0%84%EA%B5%B0

$P2_12_12_1$ crystal exhibits no permanent dipole

So , adopt octupolar systems

- turning off dipolar electrostatic interactions
- form noncentrosymmetric SHG-active bulk materials



The SHG efficiency

is given by the projection of the molecular tensor

onto the hyperellipsoid

Figure 1. Hyper-ellipsoid representation of the $\chi^{(2)}$ tensor for the $P2_12_12_1$ space group. SHG polarization (green = positive, red = negative).

net NLO tensor of the bulk material :

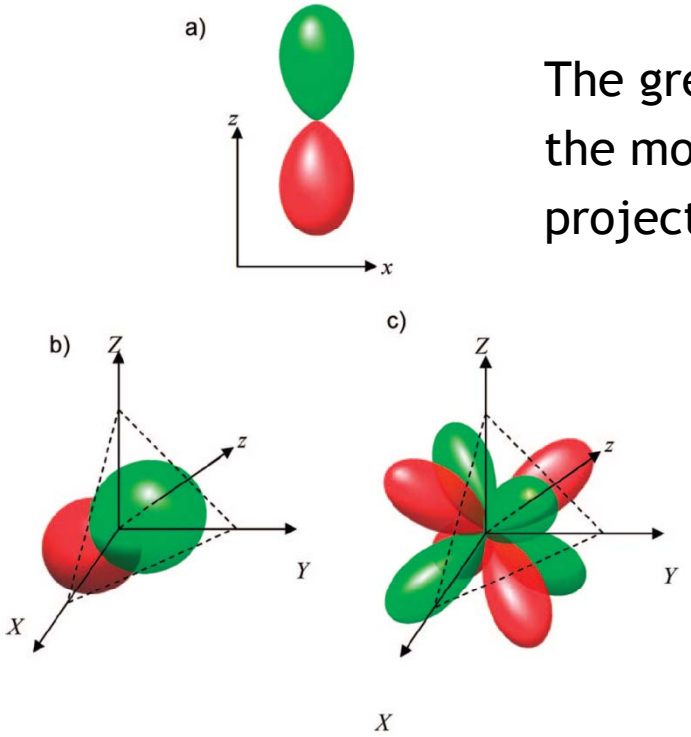
$$\chi_{IJK} \cong N_b \sum_{ijk=x,y,z} \langle R_{Ii} R_{Jj} R_{Kk} \rangle \beta_{ijk}$$

R :an element of the Euler rotation matrix describing the coordinate transformation between the molecular and macroscopic frames.

Case 1: Rod-like β_{zzz}-*Dominated NLO Chromophores.*

the maximum projection(c) :

projections of the molecular z axis onto each of the bulk X, Y, and Z axes



The greatest collective projection :

the molecular z-axis trisects all three coordinates with a projection of $1/\sqrt{3}$ along each crystallographic axis

the macroscopic chiral tensor:

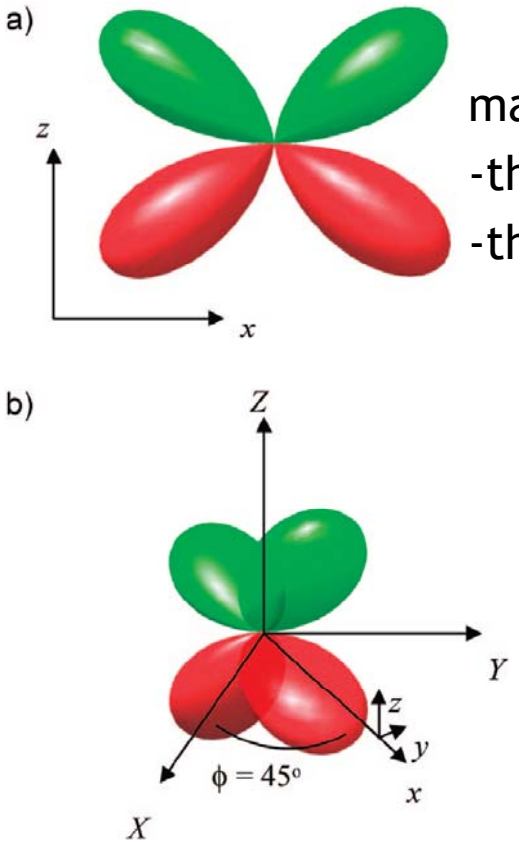
$$\chi_{XYZ} = \chi_{YZX} = \chi_{ZXY} = \frac{1}{3\sqrt{3}} N_b \beta_{zzz}$$

maximum value of $\chi^{(2)}$ tensor : 19%

per-molecule efficiency : ~ 4%

Figure 2. Hyper-ellipsoid representation of a β_{zzz} dominated chromophore(a). The optimal projection of the β_{zzz} dominated hyperellipsoid (b) on to the hyper-ellipsoid of the $P2_12_12_1$ space group (c) in Cartesian coordinates.

Case 2: Λ-Like $\beta_{xxz} = \beta_{xzx}$-Dominated Chromophores.



maximum net projection (b) :

-the z-axis of the molecule lies along one of the crystal axes

-the x-axis of the molecule bisecting the remaining crystal axes

the macroscopic chiral tensor:

$$\chi_{XYZ} = \chi_{YZX} \cong \frac{1}{2} N_b \beta_{xxz};\ \chi_{ZXY} \cong 0$$

the β_{zxx} element domination:

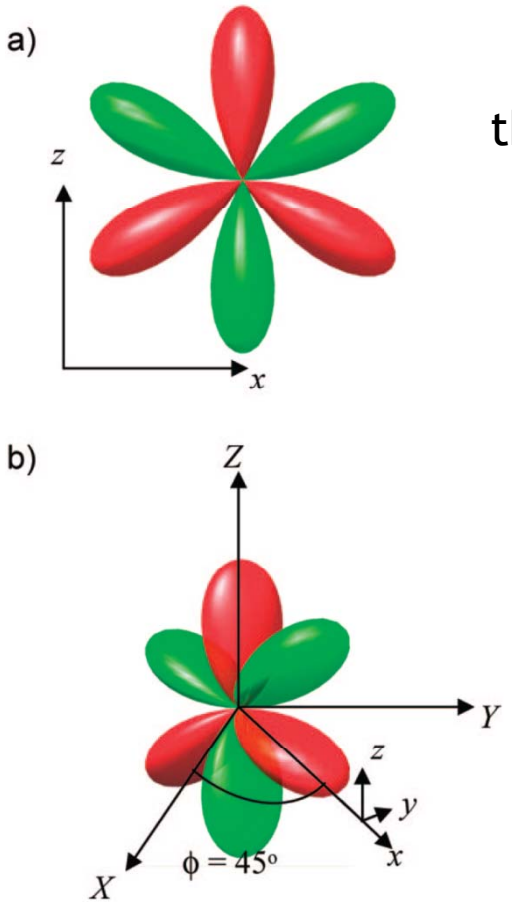
$$\chi_{XYZ} = \chi_{YZX} \cong 0;\ \chi_{ZXY} \cong \frac{1}{2} N_b \beta_{zxx}$$

Figure 3. Hyper-ellipsoid representation of a $\beta_{xxz} = \beta_{xzx}$ dominated chromophore (a) and the optimal orientation to maximize projection on to the $P2_12_12_1$ hyper-ellipsoid representation (b).

maximum value of $\chi^{(2)}$ tensor : 50%

per-molecule efficiency : 25%

Case 3: Planar Octopolar $\beta_{xxz} \cong \beta_{zxx} \cong -\beta_{zzz}$ Dominated Chromophores



the optimal orientation (b) :

- antiparallel orientation
- z-axis coparallel
- crystal axis and an azimuthal angle φ (or ψ) of ±45°.

the macroscopic chiral tensor:

$$\chi_{XYZ} = \chi_{YZX} = \chi_{ZXY} \cong \frac{1}{2} N_b \beta_{xxz}$$

maximum value of $\chi^{(2)}$ tensor : 50%

Figure 5. Hyper-ellipsoid of an octupolar chromophore (a) and the optimal projection onto the hyper-ellipsoid for the $P2_12_12_1$ space group (tridentate classes)(b).

Conclusion

- In chiral materials,
  electrostatic change of crystal structure decide according to a molecular design