

1.7. NONLINEAR OPTICAL PROPERTIES

frame. We obtain, for each wave, three equations which relate the three components (e_x, e_y, e_z) to the unit wavevector components (u_x, u_y, u_z) (Shuvalov, 1981):

$$(n^\pm)^2(e_p^\pm - u_p[u_x e_x^\pm + u_y e_y^\pm + u_z e_z^\pm]) = (n_p)^2 e_p^\pm \quad (p = x, y \text{ and } z) \quad (1.7.3.9)$$

with $(e_x^\pm)^2 + (e_y^\pm)^2 + (e_z^\pm)^2 = 1$.

The vibration planes Π^\pm relative to the eigen polarization modes \mathbf{e}^\pm are called the neutral vibration planes associated with \mathbf{u} : an incident linearly polarized wave with a vibration plane parallel to Π^+ or Π^- is refracted inside the crystal without depolarization, that is to say in a linearly polarized wave, \mathbf{e}^+ or \mathbf{e}^- , respectively. For any other incident polarization the wave is refracted in the two waves \mathbf{e}^+ and \mathbf{e}^- , which propagate with the difference of phase $(\omega/c)(n^+ - n^-)Z$.

The existence of equalities between the principal refractive indices determines the three optical classes: isotropic for the cubic system; uniaxial for the tetragonal, hexagonal and trigonal systems; and generally biaxial for the orthorhombic, monoclinic and triclinic systems [Nye (1957) and Sections 1.1.4.1 and 1.6.3.2].

1.7.3.1.2. Isotropic class

The isotropic class corresponds to the equality of the three principal indices: the index surface is a one-sheeted sphere, so $n^+ = n^-, \rho^+ = \rho^- = 0$ for all directions of propagation, and any electric field vector direction is allowed as in an amorphous material.

1.7.3.1.3. Uniaxial class

The uniaxial class is characterized by the equality of two principal indices, called ordinary indices ($n_x = n_y = n_o$); the

other index is called the extraordinary index ($n_z = n_e$). Then, according to (1.7.3.6), the index surface has one umbilicus along the z axis, $n^+(\theta = 0) = n^-(\theta = 0)$, called the optic axis, which is along the fold rotation axis of greatest order of the crystal. The two other principal axes are related to the symmetry elements of the orientation class according to the standard conventions (Nye, 1957). The ordinary sheet is spherical *i.e.* $n_o(\theta, \varphi) = n_o$, so an ordinary wave has no walk-off for any direction of propagation in a uniaxial crystal; the extraordinary sheet is ellipsoidal *i.e.* $n_e(\theta, \varphi) = [(\cos^2 \theta)/(n_o^2) + (\sin^2 \theta)/(n_e^2)]^{-1/2}$. The sign of the uniaxial class is defined by the sign of the birefringence $n_e - n_o$. Thus, according to these definitions, (n_e, n_o) corresponds to (n^+, n^-) for the positive class ($n_e > n_o$) and to (n^-, n^+) for the negative class ($n_e < n_o$), as shown in Fig. 1.7.3.2.

The ordinary electric field vector is orthogonal to the optic axis ($e_z^o = 0$), and also to the extraordinary electric field vector, leading to

$$\mathbf{e}^o(\omega_i, \theta, \varphi) \cdot \mathbf{e}^e(\omega_j, \theta, \varphi) = 0. \quad (1.7.3.10)$$

This relation is satisfied when ω_i and ω_j are equal or different and for any direction of propagation (θ, φ) .

According to these results, the coplanarity of the field vectors imposes the condition that the double-refraction angle of the extraordinary wave is in a plane containing the optic axis. Thus, the components of the ordinary and extraordinary unit electric field vectors \mathbf{e}^o and \mathbf{e}^e at the circular frequency ω are

$$e_x^o = -\sin \varphi \quad e_y^o = +\cos \varphi \quad e_z^o = 0 \quad (1.7.3.11)$$

$$e_x^e = -\cos[\theta \pm \rho^\mp(\theta, \omega)] \cdot \cos \varphi$$

$$e_y^e = -\cos[\theta \pm \rho^\mp(\theta, \omega)] \cdot \sin \varphi$$

$$e_z^e = \sin[\theta \pm \rho^\mp(\theta, \omega)] \quad (1.7.3.12)$$

Table 1.7.2.5. Nonzero $\chi^{(3)}$ coefficients and equalities between them under the Kleinman symmetry assumption

Symmetry class	Independent nonzero elements of $\chi^{(3)}$ under Kleinman symmetry
Triclinic $C_1 (1), C_i (\bar{1})$	$xxxx, xyxy = yxyx = yyyx, xzzz = zxxz = zzzx, xyzz = xzyz = xzzy = yxzz = yzxx = yzxx = zxyx = zxxz = zyxz = zzyx = zzyx, xyxz = xzyx = xzxy = yxzx = yzxx = yzxx = zxyx = zxyx = zxyx, xxzz = xzxx = xzxx = zxxx, xxxz = xxzx = xzxx = zxxx, xxyy = xyxy = xyxy = yxxx = yxxx = yxxx, xxyy = xxyy = xxyy, yyyz = yyyz = yyyz, yyyz = yyyz = yyyz, yyyz = yyyz = yyyz, zzzz$
Monoclinic $C_s (m), C_2 (2), C_{2h} (\frac{2}{m})$ (twofold axis parallel to z)	$xxxx, xyxy = yxyx = yyyx, xyzz = xzyz = xzzy = yxzz = yzxx = yzxx = zxyx = zxyx = zxyx, xxzz = xzxx = xzxx = zxxx, xxyy = xyxy = xyxy = yxxx = yxxx = yxxx, xxyy = xxyy = xxyy, yyyz = yyyz = yyyz, yyyz = yyyz = yyyz, zzzz$
Orthorhombic $C_{2v} (mm2), D_2 (222), D_{2h} (mmm)$ (twofold axis parallel to z)	$xxxx, xxzz = xzxx = xzxx = zxxx = zxxx, xxyy = xyxy = xyxy = yxxx = yxxx = yxxx, yyyz = yyyz = yyyz, yyyz = yyyz = yyyz, zzzz$
Tetragonal $S_4 (4), C_4 (4), C_{4h} (\frac{4}{m})$ $C_{4v} (4mm), D_{2d} (\bar{4}2m), D_4 (422), D_{4h} (\frac{4}{m}mm)$	$xxxx = yyyy, xyxy = yxyx = yyyx = -xxxz = -xxxz = -xxxz = -yxxx, xxzz = xzxx = xzxx = yyyz = yyyz = yyyz = zzyy = zzyy = zzyy, zzzz = zzzz = zzzz, xxyy = xyxy = xyxy = yxxx = yxxx = yxxx, yyyz = yyyz = yyyz, zzzz = zzzz = zzzz, xxyy = xyxy = xyxy = yxxx = yxxx = yxxx, zzzz = zzzz = zzzz, xxyy = xyxy = xyxy = yxxx = yxxx = yxxx, zzzz = zzzz = zzzz$
Hexagonal $C_{3h} (6), C_6 (6), C_{6h} (\frac{6}{m}), C_{6v} (6mm), D_{3h} (62m), D_6 (622), D_{6h} (\frac{6}{m}mm)$	$xxxx = yyyy = xxyy + xyxy + xyxy, xxzz = xzxx = xzxx = yyyz = yyyz = yyyz = zzyy = zzyy = zzyy = zxxx = zxxx = zxxx, xxyy = xyxy = xyxy = yxxx = yxxx = yxxx, zzzz = zzzz = zzzz$
Trigonal $C_3 (3), C_{3i} (\bar{3})$ $C_{3v} (3m), D_3 (32), D_{3d} (\bar{3}m)$ (mirror perpendicular to x) (twofold axis parallel to x)	$xxxx = yyyy = xxyy + xyxy + xyxy, xyxz = xzyx = xzyx = -xxxz = -xxxz = -xxxz = yxxx = yxxx = yxxx = yyyz = yyyz = yyyz = zzyy = zzyy = zzyy = zxxx = zxxx = zxxx = -yzyy = -yzyy = -yzyy = yxxx = yxxx = yxxx = -zyyy = zxyx = zxyx = zxyx, zzzz = zzzz = zzzz, xxyy = xyxy = xyxy = yxxx = yxxx = yxxx, xxyy = xyxy = xyxy = yxxx = yxxx = yxxx, zzzz = zzzz = zzzz, xxyy = xyxy = xyxy = yxxx = yxxx = yxxx, zzzz = zzzz = zzzz$
Cubic $T (23), T_h (m3), T_d (\bar{4}3m), O (432), O_h (m3m)$	$xxxx = yyyy = zzzz, xxzz = xzxx = xzxx = xxyy = xyxy = xyxy = yyyz = yyyz = yyyz = yxxx = yxxx = yxxx = zzyy = zzyy = zzyy = zzzz = zzzz = zzzz, zzzz = zzzz = zzzz, zzzz = zzzz = zzzz$