

## 6n. Nonlinear Optical Coefficients

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For frequency mixing in the optical region one normally uses the fact that the polarization of a material is a nonlinear function of the electric field:

$$P = \chi E(1 + a_1 E + a_2 E^2 + \dots)$$

In the limit of small electric fields this reduces to  $P = \chi E$  the term which is responsible for the linear refractive index.

Although second-harmonic generation and other mixing experiments were first done using lasers, it is not necessary that the light be coherent. Indeed, other effects such as the Kerr, Pockels, and Raman effects, are manifestations of the same nonlinearity and have been well known for some time.

The effects treated here are those due to the second-order nonlinear polarization  $P^{NL} = \chi a_1 E^2$ . They occur in acentric materials only. Taking account of the fact that nonlinear polarizability is a tensor, the nonlinear polarization is written as<sup>1</sup>  $P_i^{NL} = d_{ijk} E_j E_k$ .

Assuming that the two interacting fields are sinusoidal traveling waves with frequencies  $\omega_1$  and  $\omega_2$  and wavevectors  $k_1$  and  $k_2$ , application of basic trigonometry shows that the nonlinear polarization in general has five components: one d-c component and four components with frequencies and corresponding wave-vectors:

$$\begin{array}{cc} \omega_1 + \omega_2, k_1 + k_2 & \omega_1 - \omega_2, k_1 - k_2 \\ 2\omega_1, 2k_1 & 2\omega_2, 2k_2 \end{array} \quad \text{respectively}$$

By considering the nonlinear polarization as a perturbation to the linear source term in Maxwell's equation, it can be shown that each frequency component of the nonlinear polarization generates an electromagnetic wave with the same frequency but 90 deg out of phase [1]. Thus, if  $\omega_1 = \omega_2$ , the nonlinearity will generate a d-c electric field (optical rectification) and a wave at twice the frequency of the input (usually called the second harmonic). Similarly if either  $\omega_1$  or  $\omega_2$  is zero, the effect is the linear electro-optic effect (see Sec. 6m-5). The nonlinear polarizability in this case is related to the normally used electro-optical coefficient as  $d_{ijk}(\omega, 0, \omega) = (n^4/4\pi)\gamma_{ijk}$ , where  $n$  is the refractive index at frequency  $\omega$ .

In a matter analogous to the one in which Fresnel's equations are derived in the linear optics case, it can be shown that the nonlinear source term also generates a reflected component at the mixed frequency [2].

**6n-1. Phase Matching.** The interaction is said to be phase-matched if the wave vectors of the polarization wave and the accompanying electromagnetic wave are equal. In this case both energy and momentum are conserved:  $\omega_3 = \omega_1 + \omega_2$ ,

<sup>1</sup> Here the dummy suffix notation is adopted. Summation is implied whenever suffices are repeated on one side of an equation.

$\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2$ , and efficient energy transfer occurs. In general, because of the dispersion in the mixing crystal, one had

$$\mathbf{k}_3 = \mathbf{k}_1 + \mathbf{k}_2 + \Delta\mathbf{k} \quad (6n-1)$$

In a small-signal approximation, i.e., no significant depletion of the waves at  $\omega_1$  and  $\omega_2$ , it can be shown that the signal at  $\omega_3$  depends on  $\Delta k$  and on  $l$ , the length of the crystal, as

$$S(\omega_3) \sim \left[ \frac{l \sin(\Delta kl/2)}{\Delta kl/2} \right]^2$$

This function has a maximum for  $\Delta kl = \pi$ . The crystal length for which this maximum occurs is called the coherence length:

$$l_{\text{coh}} = \frac{\pi}{\Delta k}$$

An often-employed method of phase matching [3] utilizes the fact that in a uniaxial birefringent crystal the index of refraction for an extraordinary ray,  $n^{\text{ext}}$ , can be made to vary between the extraordinary index  $n_e$  and the ordinary index  $n_o$ , by varying the angle  $\theta$  between the wave normal and the optical axis:

$$n^{\text{ext}} = \frac{n_o n_e}{(n_e^2 \sin^2 \theta + n_o^2 \cos^2 \theta)^{1/2}}$$

In this method all three waves are propagated with parallel-wave normals. This reduces Eq. (6n-1) to the form

$$\omega_3 n_3 = \omega_1 n_1 + \omega_2 n_2 + \omega_3 \Delta n$$

Now one or two of the waves are polarized in a plane parallel to the optical axis (extraordinary polarization), and the remaining one(s) are polarized as ordinary rays. By choosing the correct value of  $\theta$  the refractive indices of the extraordinary rays are adjusted to give  $\Delta n = 0$ . In this arrangement the direction of the extraordinary ray is not parallel to its wave normal, unless  $\theta = 90$  deg, thus causing the length in which all three waves overlap to be finite. For a more detailed treatment, including the effects of crystal symmetry, see Midwinter and Warner [4].

In a modification of this method all three waves are propagated in a direction perpendicular to the optical axis, and the temperature of the crystal is varied to adjust the refractive indices to the values necessary to give  $\Delta n = 0$ . This method is often referred to as temperature tuning. It has the advantage that the ray directions of all the waves remain parallel [5]. Also, the variation of index with angle of propagation is smallest when  $\theta = 90$  deg, allowing for sharper focusing of the beams. A d-c electric field can be applied to "fine tune" the phase-matching condition, using the electro-optic effect [6].

Phase matching in biaxial crystal has been treated by Hobden [7].

**6n-2. Symmetry and Contraction of  $d_{ijk}$ .** Armstrong [8] et al. have shown that  $d_{ijk}(\omega_1, \omega_2, \omega_3) = d_{kji}(\omega_3, \omega_2, \omega_1) = d_{jik}(\omega_2, \omega_1, \omega_3)$ . This reduces the number of independent coefficients from 81 to 27. It also shows that the last two indices are interchangeable:  $d_{ijk} = d_{ikj}$ . It is therefore possible to write the tensor in a contracted form:  $d_{il}$ , with  $l$  running from 1 to 6. Now  $d_{il} = d_{ijl}$  for  $k = j$  and  $d_{il} = \frac{1}{2}(d_{ijk} + d_{ikj})$  for  $k \neq j$ . Equation (6n-2) shows the normally used, contracted matrix with the column matrix on which it operates.

$$\begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_y E_x \\ 2E_x E_z \\ 2E_x E_y \end{pmatrix} \quad (6n-2)$$

Note that the form of the matrix is very much the same as the form of the piezoelectric matrix, except that here the 4, 5, 6 columns operate on  $2E_1E_2$ , etc. In other words, the usual factor of 2 is included in the field upon which the matrix operates, instead of in the matrix itself. This definition is not uniformly accepted in the literature, and caution should be exercised.

**6n-3. Symmetry of  $d_{ik}$ , Kleinman's Conjecture.** The nonlinearity of the polarization must be invariant to those symmetry operations which transform the crystal into itself. For a specific crystal class the matrix of the second-order susceptibility is homologous with the piezoelectric matrix, except for the factor 2 mentioned above. The values of the matrix elements are of course not related to those of the piezoelectric matrix.

For second-harmonic generation Kleinman has suggested that in nondispersive nonabsorbing media a second symmetry condition obtains [9]. This condition allows all three indices  $i$ ,  $j$ , and  $k$  in the coefficient  $d_{ijk}$  to be freely interchanged. In the absence of any other symmetry conditions the number of independent coefficients is then reduced to ten:

$$\begin{array}{cccccc} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{16} & d_{22} & d_{23} & d_{24} & d_{14} & d_{12} \\ d_{15} & d_{24} & d_{33} & d_{23} & d_{13} & d_{14} \end{array}$$

Combined with the symmetry conditions which govern the piezoelectric tensor, this condition reduces the number of independent coefficients even further than in the piezoelectric matrix. For example, in quartz the normal symmetry conditions give two independent coefficients,  $d_{11} = -d_{12} = -d_{26}$ , and  $d_{14} = -d_{25}$ , with all the other coefficients = 0. Kleinman's condition requires  $d_{14} = d_{25}$ , and so  $d_{14} = 0$ .

The allowed values of the nonlinear optical coefficients for the crystal classes listed in Table 6n-1 are:

Crystal Class	Coefficients
4mm, 6mm	$d_{31} = d_{32}; d_{33}; d_{24} = d_{15}$
3m	$d_{21} = -d_{22} = d_{16}; d_{24} = d_{15}; d_{31} = d_{32}; d_{33}$
mm2	$d_{31}; d_{32}; d_{33}; d_{24}; d_{15}$
42m	$d_{14} = d_{25}; d_{36}$
43m	$d_{14} = d_{25} = d_{36}$
222	$d_{14}; d_{25}; d_{36}$
32	$d_{11} = -d_{12} = -d_{26}; d_{14} = -d_{25}$

**6n-4. Output Power.** In a small-signal approximation the output power is given by [10]

$$S(\omega_3) = S(\omega_1)S(\omega_2) \frac{32\pi^3\omega_3^2 l^2}{c^3 n_1 n_2 n_3} d_{\text{eff}}^2 \frac{\sin \Delta kl/2}{\Delta kl/2} \quad (6n-3)$$

Here  $S(\omega_n)$  is the power at the frequency  $\omega_n$  in ergs  $\text{cm}^{-2}$ ,  $d_{\text{eff}}$  is the nonlinear coefficient multiplied by the terms introduced by the matrix because of the direction of propagation in the medium,  $l$  is the length of the crystal, and  $n_i$  is the index at the frequency  $\omega_i$ .

Since  $d_{\text{eff}}$  is most often given in esu, but intensities are usually expressed in watts  $\text{cm}^{-2}$ , a more convenient equation is [11]

$$P(\omega_3) = \frac{13.04 P(\omega_1)P(\omega_2)d_{\text{eff}}^2 l^2}{n_1 n_2 n_3 \lambda^3} \left( \frac{\sin \Delta kl/2}{\Delta kl/2} \right)^2 \quad (6n-4)$$

where  $l$  is the crystal length, and  $\lambda$  the free-space wavelength, both in cm.  $P(\omega)$  is in watts  $\text{cm}^{-2}$ , and  $d_{\text{eff}}$  is in esu. Equations (6n-3) and (6n-4) are for single-mode inputs.

In esu the dimension of the nonlinear coefficient is  $\text{cm}/\text{stat. volt}$ . In mks units this becomes meters/volt. The conversion from esu to mks units is given by  $d(\text{mks}) =$

TABLE 6n-1. NONLINEAR OPTICAL COEFFICIENTS

Material	Class	$\lambda$	Coefficients in $10^{-9}$ esu			Ref.	Index data
			$d_{15}$	$d_{31}$	$d_{33}$		
BaTiO <sub>3</sub> .....	4mm	1.06	57 ± 19	60 ± 20	22 ± 7	13	15
K <sub>3</sub> LiNbO <sub>3</sub> .....	4mm	1.06	.....	15 ± 2	20 ± 2	15	
ZnO.....	6mm	1.06	7.6 ± 2.5	7 ± 2	16 ± 7	13	
CdS.....	6mm	1.06	57 ± 19	53 ± 9	102 ± 32	13	
ZnS.....	6mm	10.6	69 ± 17	63 ± 15	105 ± 30	16	
		1.06	.....	.....	25 ± 8	17	
CdSe.....	6mm	10.6	51 ± 20	45 ± 15	89 ± 30	16	
		1.06	.....	.....	147 ± 49	17	
		10.6	74 ± 18	68 ± 15	130 ± 30	16	
LiNbO <sub>3</sub> *.....	3m	1.06	$d_{31}$ 22 ± 2	$d_{32}$ 9 ± 5	$d_{33}$ 145 ± 27	18, 19, 36	20, 18
Ag <sub>3</sub> AsS <sub>3</sub> (proustite).....	3m	1.15	48 ± 12	80 ± 20	.....	21	21
Ba <sub>2</sub> NaNb <sub>6</sub> O <sub>15</sub> ...	mm2	1.06	$d_{15}$ 25 ± 8	$d_{24}$ 22 ± 2	$d_{32}$ 31 ± 2	22	22

  

Material	Class	$\lambda$	Coefficients in $10^{-9}$ esu		Ref.	Index data
			$d_{14}$	$d_{36}$		
KH <sub>2</sub> PO <sub>4</sub> (KDP).....	42m	1.06	1.6 ± 0.5	.....	13	23
		1.15	.....	1.6 ± 0.4	35	
KD <sub>2</sub> PO <sub>4</sub> .....	42m	1.06	1.5 ± 0.4	1.5 ± 0.4	13	23
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> .....	42m	1.06	1.36 ± 0.16	.....	13	
KH <sub>2</sub> AsO <sub>4</sub> .....	42m	0.6328	.....	1.36 ± 0.16	24	
		1.06	1.8 ± 0.5	1.7 ± 0.5	13	
InAs.....	43m	10.6	1000 ± 300	.....	16	31
CdTe.....	43m	10.6	400 ± 150	.....	16	
ZnS.....	43m	1.06	.....	80 ± 24	17	
		10.6	73 ± 20	.....	16	
ZnSe.....	43m	1.06	.....	105 ± 32	17	31
		10.6	187 ± 70	.....	16	
ZnTe.....	43m	1.06	.....	353 ± 111	17	31
		10.6	220 ± 80	.....	16	
GaP.....	43m	1.06	238 ± 40	136 ± 40	13, 17	32
GaAs.....	43m	1.06	760 ± 190	827 ± 240	13, 17	
		10.6	880 ± 300	.....	.....	
N <sub>4</sub> (CH <sub>2</sub> ) <sub>6</sub> .....	43m	1.06	16 ± 5	.....	25	
Ammonium oxalate....	222	0.6943	$d_{14}$ 1.25	$d_{36}$ .....	26	
C <sub>6</sub> H <sub>5</sub> COHN— CH <sub>2</sub> CO <sub>2</sub> H.....	222	0.6943	6.8	.....	27	
HIO <sub>3</sub> ( $\alpha$ -iodic acid)....	222	1.15	15 ± 6	.....	35	28
SiO <sub>2</sub> (quartz).....	32	1.06	$d_{11}$ 1.33 ± 0.4	.....	13	33
Se.....	32	10.6	190 ± 100	.....	16	
Te.....	32	10.6	12,700	.....	29	29
AlPO <sub>4</sub> .....	32	1.06	1.37 ± 0.42	.....	13	
HgS (cinnabar).....	32	10.6	150 ± 50	.....	30	30
K <sub>2</sub> S <sub>2</sub> O <sub>6</sub> .....	32	0.6943	0.50	.....	34	34

\* The values of  $d_{31}$  and  $d_{32}$  in LiNbO<sub>3</sub> have opposite signs.

$d(\text{esu})/3 \times 10^4$ . It is sometimes given as  $d(\text{mks}) = 4\pi d(\text{esu})/3 \times 10^4$ . In the latter case the  $d(\text{mks})$  is the nonlinear susceptibility, and the nonlinear polarization is given by

$$P = \epsilon_0 dEE$$

where  $\epsilon_0$  is the permittivity of free space.

Some authors include  $\epsilon_0$  in the coefficient. Then the conversion from esu to mks becomes

$$d(\text{mks}) = 3.68 \times 10^{-16} d(\text{esu})$$

**6n-5. Coefficients for Second-harmonic Generation.** A number of nonlinear coefficients for second-harmonic generation are listed in Table 6n-1. In all cases these have been measured in experiments generating the second harmonic of the wavelength listed. Most of the reported measurements were made relative to a "known" crystal. The values given in Table 6n-1 are absolute values. They were all calculated from these relative measurements, using the listed coefficient  $d_{11}$  for ADP. The reference for each crystal is given in the first reference column. The second reference column gives available index-of-refraction data.

In selecting a crystal for a particular application, it should be borne in mind that a large nonlinear coefficient is not the only requirement for efficient generation. It should also be possible to grow crystals of optical quality to the required size, and the material should be transparent at all frequencies involved. Another danger is that the crystal may suffer optical damage from the large incident intensities. This type of damage was first observed in  $\text{LiNbO}_3$  [12].

**6n-6. Miller's Rule.** Miller has found empirically that if  $d_{ijk}^{\omega_1\omega_2\omega_3}$  is written as

$$d_{ijk}^{\omega_1\omega_2\omega_3} = x_{ii}^{\omega_1} x_{jj}^{\omega_2} x_{kk}^{\omega_3} \Delta_{ijk}$$

where  $x_{ii}^{\omega_1}$  is the  $ii$  component of the linear optical susceptibility at frequency  $\omega_1$ , then the allowed components of  $\Delta_{ijk}$  for all materials have the same magnitude [13,14]. This provides a helpful pointer to good new materials.

**6n-7. Material Evaluation.** A useful technique for evaluating materials in powder form has been developed by Kurtz and Perry [37].

#### References

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