Optical Properties of Highly Transparent Solids

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SECOND-HARMONIC GENERATION OF INTENSE LASER LIGHT IN TRANSPARENT CENTROSYMMETRIC SOLIDS

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The authors analyze the feasibility of second-harmonic generation (SHG) intensity amplification in centrosymmetric solids by:
1. Nonlinear spatial dispersion, related with electric and magnetic multipolar transitions;
2. Changes in nonlinear susceptibilities self-induced by strong laser light intensity;
3. Lowering of the intrinsic crystal symmetry e.g. inversion centre destruction by a DC electric or magnetic field, or crossed fields;
4. Coupling between self-light-intensity dependent effects and DC applied-field induced effects.
Supplementing hitherto considered SHG mechanisms, these new processes are described in terms of 5-th and 6-th rank polar and axial tensors of electro-electric and magneto-electric nonlinear susceptibilities. The nonzero and independent elements of these new tensors are calculated, thus pinpointing those classes of centrosymmetric crystals where SHG can occur with amplified intensity.

INTRODUCTION

Terhune et al [1] observed weak second-harmonic generation (SHG) in the light transmitted by calcite crystal, which has a centre of symmetry. That earliest experiment was repeated by Bjorkholm and Siegman [2] , who compared the SHG in-

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tensities from calcite and ADP crystal. Wang and Dumiński [3] observed SHG in transmission through thin platelets of glass and LiF. Bloembergen et al [4] studied SHG in reflection from a medium with inversion symmetry. This kind of SHG both in transmitted and reflected light was hitherto attributed to electric quadrupole and magnetic dipole polarization [5-10].

The study of SHG in bodies exhibiting a phase transition from a state without centre of symmetry to a centrosymmetric state and vice versa e.g. under the influence of a DC electric field [11] is of the greatest interest [11, 12]. Recently, Vogt [13] performed such SHG studies on Sodium Nitrite at the temperature transition from the ferroelectric state, when the symmetry is m2m, to the paraelectric state, in which the crystal as a whole has a centre of inversion with the symmetry mmm. Rabin [14] analyzed the conditions for SHG provided by the introduction of lattice defects into centrosymmetric crystals.

It is a well known fact that in the process of light self-focusing the refractive index and thus the susceptibility of the medium become light-intensity dependent [15]. It is the aim of this paper to show that in the process of SHG as well, when using strong laser light, the nonlinear susceptibility tensors become functions of the light intensity. We suggested and considered this earlier [16] with regard to SHG by isotropic electrically polarized bodies. Since self-induced nonlinearities occur in all bodies to a larger or lesser degree, the nonlinear susceptibilities of materials determined by the method of harmonics generation [17,18] depend on the light intensity itself.

We shall restrict our discussion to SHG in centrosymmetric materials, in which the self-induced light-intensity dependence of the nonlinear magneto-electric dipolar and electric quadrupole susceptibilities are described, respectively, by a 5-th rank axial tensor of dipolar magneto-electric susceptibility and a 6-th rank polar tensor of electric-electric quadrupole susceptibility. Besides frequency dispersion, we take into account the nonlinear spatial dispersion derived in a previous theory of multipole transitions [19], induced in quantal systems by strong electromagnetic fields. We also discuss amplification in SHG intensity, due to inversion centre destruction by an external DC electric or magnetic field, and able to exhibit coupling with optically self-induced SHG amplification.

SHG IN THE PRESENCE OF INVERSION CENTRE

Quite generally, the total electric polarization of a medium at the space-time point $(\underline{r},t)$ is given by the multipole expansion [19]:

$$\underline{P}_e(\underline{r},t) = \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{(2m-1)!!} \nabla^{m-1}[m-1]\, \underline{P}_e^{(m)}(\underline{r},t), \qquad (1)$$

$\underline{P}_e^{(m)}(\underline{r},t)$ denoting 2^m-pole electric polarization, and $[m-1]$ an $m-1$-fold contraction between the spatial differential operator ∇^{m-1} and the m-vector $\underline{P}_e^{(m)}$. On the other hand, the electric polarization vector is a function of the electric field:

$$\underline{E}(\underline{r},t) = \underline{E}(\underline{r},t)e^{-i\omega t} = \underline{E}(\omega,\underline{k})\exp[i(\underline{k}\cdot\underline{r} - \omega t)], \qquad (2)$$

and of the similarly defined magnetic field $\underline{B}(\underline{r},t)$ of a light wave, of frequency ω and propagation $\underline{k}$.
SHG is defined by second-order polarization, of the form [19]:

$$\overset{(2)}{\underline{P}}{}_e^{(m)}(\underline{r},t) = \sum_{n=1}^{\infty}\sum_{s=1}^{\infty} \frac{\exp(-i2\omega t)}{(2n-1)!!(2s-1)!!} \cdot$$

$$\Big\{ {}^{(m)}_{\ e}\underline{\chi}^{(n+s)}_{ee}(2\omega)[n+s][\nabla^{n-1}\underline{E}(\underline{r},\omega)][\nabla^{s-1}\underline{E}(\underline{r},\omega)] +$$

$$+ {}^{(m)}_{\ e}\underline{\chi}^{(n+s)}_{em}(2\omega)[\nabla^{n-1}\underline{E}(\underline{r},\omega)][\nabla^{s-1}\underline{B}(\underline{r},\omega)] + \dots\Big\}, \qquad (3)$$

where ${}^{(m)}_{\ e}\underline{\chi}^{(n+s)}_{ee}(2\omega)$ is a tensor of 2-nd order electric multipole susceptibility at frequency 2ω taking into account all 2^{n+s}-pole electric transitions. Likewise, ${}^{(m)}_{\ e}\underline{\chi}^{(n+s)}_{em}(2\omega)$ is a tensor of electric multipole susceptibility containing contributions from 2^n-pole electric and 2^s-pole magnetic transitions, in conformity with the quantum-mechanical formula:

$$ {}^{(m)}_{\ e}\underline{\chi}^{(n+s)}_{em}(2\omega) = \frac{\varrho}{\hbar^2} S(n,s) \sum_{abcd} \varrho_{ab}$$

$$\Big\{ \frac{\langle a|\underline{M}_e^{(m)}|c\rangle\langle c|\underline{M}_e^{(n)}|d\rangle\langle d|\underline{M}_m^{(s)}|b\rangle}{(\omega_{cb}+2\omega+i\Gamma_{cb})(\omega_{db}+\omega+i\Gamma_{db})} +$$

$$+ \frac{\langle a|\underline{M}_e^{(n)}|c\rangle\langle c|\underline{M}_e^{(m)}|d\rangle\langle d|\underline{M}_m^{(s)}|b\rangle}{(\omega_{ca}-\omega-i\Gamma_{ca})(\omega_{db}+\omega+i\Gamma_{db})} +$$

$$+ \frac{\langle a|\underline{M}_e^{(n)}|c\rangle\langle c|\underline{M}_m^{(s)}|d\rangle\langle d|\underline{M}_e^{(m)}|b\rangle}{(\omega_{ca}-\omega-i\Gamma_{ca})(\omega_{da}-2\omega-i\Gamma_{da})}\Big\}, \qquad (4)$$

where ϱ is the number density of the medium, ϱ_{ab} the statistical matrix for the transition $a \to b$ with Bohr frequency ω_{ab} and relaxation time Γ_{ab}^{-1}, and $\underline{M}_e^{(m)}$, $\underline{M}_m^{(s)}$ the 2^m-pole electric and 2^s-pole magnetic moment operator of the quantal system. On writing $\underline{M}_e^{(s)}$ instead of $\underline{M}_m^{(s)}$ in (4), we get an expression for the susceptibility tensor ${}^{(m)}_{\ e}\underline{\chi}^{(n+s)}_{ee}(2\omega)$.

Eqs (1) and (2) define the influence of spatial dispersion of all orders on SHG. At very high light intensity, the electric polarization (1) at 2ω contains contributions of higher even orders besides that of 2-nd order (3). Thus we can write the total electric polarization at 2ω, in a satisfactory approximation, as:

$$P_{ei}(2\omega,\underline{r}) = \chi^{eee}_{ijk}(2\omega,\underline{k},I)E_j(\omega,\underline{r})E_k(\omega,\underline{r}) + \\ + \chi^{eem}_{ijk}(2\omega,\underline{k},I)E_j(\omega,\underline{r})B_k(\omega,\underline{r}) + \dots, \qquad (5)$$

Hence, the tensors of nonlinear 2-nd order electric-electric and electro-magnetic susceptibility, which are the source of SHG, depend in general not only on frequency dispersion ω but also on spatial dispersion $\underline{k}$ and on the incident light intensity $I=E(\omega,\underline{r})E^*(\omega,\underline{r})$. For bodies having a centre of inversion we thus get in a satisfactory approximation:

$$\chi^{eee}_{ijk}(2\omega,\underline{k},I) = i\Big\{\chi^{eeek}_{ijkl}(2\omega) + \chi^{eeekkk}_{ijklmn}(2\omega)k_m k_n + \\ + \chi^{eeekee}_{ijklmn}(2\omega)E_n(\omega,\underline{k})E^*_m(\omega,\underline{k}) + \dots\Big\}k_l, \qquad (6)$$

$$\chi^{eem}_{ijk}(2\omega,\underline{k},I) = \chi^{eem}_{ijk}(2\omega) + \chi^{eemkk}_{ijklm}(2\omega)k_l k_m + \\ + \chi^{eemee}_{ijklm}(2\omega)E_l(\omega,\underline{k})E^*_m(\omega,\underline{k}) + \dots, \qquad (7)$$

The expansions (6) and (7) are expressed formally in such a manner that the individual susceptibility tensors contain the respective multipole transition contributions resulting from Eq. (4); however, for brevity, we omit the numerical expansion coefficients. E.g., the polar tensor χ^{eeek}_{ijkl} consists of the nonlinear electric dipole susceptibility ${}^{(1)}\underline{\chi}^{(1+2)}_{e\,ee}$ with electric dipole-quadrupole transition and of the electric quadrupole susceptibility ${}^{(2)}\underline{\chi}^{(1+1)}_{e\,ee}$ with electric dipole-dipole transitions. The polar 6-th rank tensor χ^{eeekkk}_{ijklmn} consists in general of successive multipolar susceptibilities with the appropriate multipolar transitions.

Non-zero and independent elements of the polar tensor χ^{eeek}_{ijkl} are listed in Table I. The numbers of nonzero and mutually independent elements of the remaining tensors of Eqs (6) and (7) for centrosymmetric classes are given in Table II. The axial tensor elements χ^{eem}_{ijk} and χ^{eeem}_{ijklm} have been tabulated previously for all classes [20].

For fields of the form (2), Maxwell's equations yield:

Table 1.
Non-zero and independent elements of the polar tensor χ^{eeek}_{ijkl} for all centrosymmetric crystallographical classes.

Class	Elements χ^{eeek}_{ijkl}
$\bar{1}$	A≡xxxx,yyyy,zzzz,xxyy,yyxx,xyxy,yxyx,xyyx,yxxy,xxzz,zzxx, xzxz,zxzx,xzzx,zxxz,yyzz,zzyy,yzyz,zyzy,yzzy,zyyz; B≡xxxy,xxyx,xyxx,yxxx,yyyx,yyxy,yxyy,xyyy,xzzy,xzyz,xyzz, yzzx,yzxz,yxzz,zzxy,zxzy,zxyz,zzyx,zyzx,zyxz; C≡xxxz,xxzx,xzxx,zxxx,zzzx,zzxz,zxzz,xzzz,xyyz,xyzy,xzyy, zyyx,zyxy,zxyy,yyxz,yxyz,yxzy,yyzx,yzyx,yzxy,yyyz,yyzy, yzyy,zyyy,zzzy,zzyz,zyzz,yzzz,xxyz,xyxz,xyzx,xxzy,xzxy, xzyx,yzxx,yxzx,yxxz,zyxx,zxyx,zxxy;
2/m	A and B
mmm	A

4/m	D≡xxxx=yyyy,zzzz,xxyy=yyxx,xyxy=yxyx,xyyx=yxxy,xxzz=yyzz,
	xzxz=yzyz,xzzx=yzzy,zzxx=zzyy,zxzx=zyzy,zxxz=zyyz;
	E≡zzxy=-zzyx,zxyz=-zyxz,xzzy=-yzzx,xyzz=-yxzz,zxzy=-zyzx,
	xzyz=-yzxz,xxxy=-yyyx,xxyx=-yyxy,xyxx=-yxyy,yxxx=-xyyy;

4/mmm	D

$\bar{3}$	F≡zzzz,xxxx=yyyy=xxyy+xyxy+xyyx,xxyy=yyxx,xyxy=yxyx,xyyx=
	=yxxy,xxzz=yyzz,xzxz=yzyz,xzzx=yzzy,zzxx=zzyy,zxzx=zyzy
	zxxz=zyyz;
	G≡xxxy=-yyyx=-(xxyx+xyxx+yxxx),xxyx=-yyxy,xyxx=-yxyy,
	yxxx=-xyyy,zzxy=-zzyx,zxyz=-zyxz,xzzy=-yzzx,xyzz=-yxzz,
	zxzy=-zyzx,xzyz=-yzxz;
	H≡xxxz=-xyyz=-yxyz=-yyxz,xxzx=-xyzy=-yxzy=-yyzx,xzxx=
	=-xzyy=-yzxy=-yzyx,zxxx=-zxyy=-zyxy=-zyyx;
	J≡yyyz=-yxxz=-xyxz=-xxyz,yyzy=-yxzx=-xyzx=-xxzy,yzyy=
	=-yzxx=-xzyx=-xzxy,zyyy=-zyxx=-zxyx=-zxxy;

$\bar{3}$m	F and J
6/m	F and G
6/mmm	F
m3	L≡xxxx=yyyy=zzzz; M≡xxyy=zzxx=yyzz; N≡yyxx=xxzz=zzyy; P≡xyxy=zxzx=yzyz; Q≡yxyx=xzxz=zyzy; R≡xyyx=zxxz=yzzy; S≡yxxy=xzzx=zyyz;
m3m	L, M=N, P=Q and R=S,
Y_h, K_h	L=xxyy+xyxy+xyyx, M=N, P=Q and R=S,

$$B_k(\omega,\underline{r}) = -\left(\frac{c}{\omega}\right)\varepsilon_{klm}E_l(\omega,\underline{r})\,k_m, \tag{8}$$

and Eq. (5) can be re-written in the form:

$$P_{ei}(2\omega,\underline{r}) = \chi^{T}_{ijk}(2\omega,\underline{k},I)\,E_j(\omega,\underline{r})\,E_k(\omega,\underline{r}), \tag{9}$$

where we have introduced the tensor of total nonlinear 2-nd order susceptibility:

$$\chi^{T}_{ijk}(2\omega,\underline{k},I) = \chi^{eee}_{ijk}(2\omega,\underline{k},I) - \left(\frac{c}{\omega}\right)\chi^{eem}_{ijl}(2\omega,\underline{k},I)\,\varepsilon_{lkm}k_m, \tag{10}$$

with ε_{lkm} — the Levi-Cività antisymmetric tensor.

REMOVAL OF SYMMETRY CENTRE BY DC FIELDS

An electric field $\underline{E}^o$ or magnetic field $\underline{B}^o$ acts on a body in a way to lower its symmetry, i.a. by removal of its centre of symmetry, thus leading to an enhancement of the SHG power from centrosymmetric crystals [1,2]. The nonlinear susceptibility tensors of Eq. (5) now become moreover functions of $\underline{E}^o$ or $\underline{B}^o$, e.g. $\chi^{eee}_{ijk}(2\omega,\underline{k},I,\underline{E}^o)$. If the DC electric field $\underline{E}^o$ applied to the centrosymmetric crystal is not excessively strong one can write, besides (6) and (7), the following expansions:

$$\chi^{eee}_{ijk}(2\omega,\underline{k},I,\underline{E}^o) = \chi^{eeee}_{i(jk)l}(2\omega)E^o_l + \chi^{eeekke}_{ijklmn}(2\omega)k_lk_mE^o_n +$$

$$+ \chi^{eeeeee}_{i(jk)(lmn)}(2\omega)E^o_lE^o_mE^o_n + i\chi^{eeekee}_{ijkl(mn)}(2\omega)k_lE^o_mE^o_n +$$

$$+ \chi^{eeeeee}_{i(jk)lmn}(2\omega)E_l(\omega,\underline{k})\,E^*_m(\omega\underline{k})E^o_n + \ldots, \tag{11}$$

$$\chi^{eem}_{ijk}(2\omega,\underline{k},\underline{E}^o) = \chi^{eemee}_{ijk(lm)}(2\omega)E^o_lE^o_m + i\chi^{eemke}_{ijklm}(2\omega)k_lE^o_m + \ldots, \tag{12}$$

Hitherto, in the interpretation of results of DC electric-field induced SHG studies, only the first term of (11) was used.

If the centrosymmetric body is immersed in a DC magnetic field $\underline{B}^o$, the expansions (6) and (7) have to be supplemented with these:

$$\chi^{eee}_{ijk}(2\omega,\underline{k},\underline{B}^o) = i\chi^{eeekm}_{ijklm}(2\omega)k_lB^o_m + i\chi^{eeekmm}_{ijkl(mn)}(2\omega)k_lB^o_mB^o_n + \ldots, \tag{13}$$

$$\chi_{ijk}^{eem}(2\omega,\underline{k},I,\underline{B}^o) = \chi_{ijkl}^{eemm}(2\omega)B_l^o + \chi_{ijk(lm)}^{eemmm}(2\omega)B_l^oB_m^o +$$

$$+ \chi_{ijklmn}^{eemmee}(2\omega)B_l^oE_m(\omega,\underline{k})E_n^*(\omega,\underline{k}) + \chi_{ijklmn}^{eemkkm}(2\omega)k_lk_mB_n^o + \ldots, \quad (14)$$

The only available SHG study in the presence of a DC magnetic field is for InSb [21] —— a material of the class $\bar{4}3m$ without centre of symmetry.

SHG observations can also be performed in crossed DC electric and magnetic fields [22]. One now has the nonlinear susceptibilities:

$$\chi_{ijk}^{eee}(2\omega,\underline{k},\underline{E}^o,\underline{B}^o) = \chi_{i(jk)lm}^{eeeem}(2\omega)E_l^oB_m^o + \chi_{i(jk)l(mn)}^{eeeemm}(2\omega)E_l^oB_m^oB_n^o \quad (15)$$

$$\chi_{ijk}^{eem}(2\omega,\underline{k},\underline{E}^o,\underline{B}^o) = i\chi_{ijklmn}^{eemkem}(2\omega)k_lE_m^oB_n^o + \chi_{ijkl(mn)}^{eemmee}(2\omega)B_l^oE_m^oE_n^o, \quad (16)$$

The expansions (11) - (16) involve, in addition to the well known tensors χ_{ijkl}^{eeee}, χ_{ijkl}^{eemm}, χ_{ijklm}^{eeeem} and the ones discussed in Section 2, some new polar and axial tensors of ranks 5 and 6 for which the numbers of nonzero and independent tensor elements are given, for centrosymmetric bodies, in Table III.

DISCUSSION AND CONCLUSIONS

By Eqs (5) - (16), the observation and amplification of SHG from centrosymmetric bodies requires that various new mechanisms, related with nonlinear susceptibility tensors of ranks 5 and 6, shall be taken into account. This surely complicates the problem considerably. However, we now have at our disposal the experimental possibilities of determining the values of higher nonlinear susceptibilities [23]. Even when these values are not available, Tables I - III and Eqs (5) - (16) still give us the possibility of ajusting the natural configuration of the crystal and the direction of incidence and polarisation of the light beam so as to achieve the maximal SHG signal.

Existing studies [3,4,24] show that second-harmonic radiation is generated chiefly by the surface layer, where field inhomogeneities are far larger than in the bulk of the crystal. This does not apply to plastic crystals or to ones with structural phase transitions [11 - 13], where conditions favor the recurrence of the SHG processes considered by us. However, in bodies with natural and induced optical inhomogeneities, not only SHG but moreover second-harmonic scattering (SHS) takes place [25 - 28]. In general, both in SHG and SHS, a periodic spatial modulation of the nonlinear susceptibilities intervenes [29].

Table II.
The number of non-zero (N) and independent (I) elements of the nonlinear susceptibility tensors of Eqs. (6) and (7). Symmetricity in indices is denoted by parenthesses (i...).

Class	χ^{eem}_{ijk}		$\chi^{eemkk}_{(il)(jm)k}$		χ^{eemee}_{ijklm}		$\chi^{eeekee}_{ij(kl)mn}$		$\chi^{eeekkk}_{(il)(jm)(kn)}$	
	N	I	N	I	N	I	N	I	N	I
$\bar{1}$	27	27	243	108	243	243	729	486	729	216
2/m	13	13	121	52	121	121	365	244	365	112
mmm	6	6	60	24	60	60	183	123	183	60
4/m	13	7	117	26	121	61	363	122	351	56
4/mmm	6	3	56	11	60	30	183	62	183	32
$\bar{3}$	21	9	229	36	233	81	715	162	711	72
$\bar{3}$m	10	4	112	16	116	40	359	82	359	40
6/m	13	7	117	20	121	51	363	92	359	40
6/mmm	6	3	56	8	60	25	183	47	183	24
m3	6	2	60	8	60	20	183	41	183	20
m3m	6	1	48	3	60	10	183	21	183	12
Y_h, K_h	6	1	48	1	60	6	183	10	183	6

Table III.
The number of non-zero (N) and independent (I) elements of the nonlinear susceptibility tensors of Eqs. (11) – (16). Symmetricity in indices is denoted by parenthesses (i...).

Class	$\chi^{eeekm}_{ij(kl)m}$		χ^{eemmee}_{ijklmn}		$\chi^{eeeeee}_{i(jk)lmn}$		$\chi^{eeeemm}_{i(jk)l(mn)}$		$\chi^{eeeeee}_{i(jk)(lmn)}$	
	N	I	N	I	N	I	N	I	N	I
$\bar{1}$	243	162	729	729	729	486	729	324	729	180
2/m	121	80	365	365	365	244	365	164	365	92
mmm	60	39	183	183	183	123	183	84	183	48
4/m	119	40	365	183	363	122	361	82	357	46
4/mmm	58	19	183	92	183	62	183	43	183	25
$\bar{3}$	231	54	717	243	715	162	713	108	709	60
$\bar{3}$m	114	26	359	122	359	82	359	56	359	32
6/m	119	32	365	143	363	92	361	60	357	32
6/mmm	58	15	183	72	183	47	183	32	183	18
m3	60	13	183	61	183	41	183	28	183	16
m3m	54	6	183	31	183	21	183	15	183	9
Y_h, K_h	54	3	183	16	183	10	183	7	183	4

Surely some progress in the SHG study of centrosymmetric crystals can be expected from the latest observations by Yu and Alfano [30] of double- and triple-photon scattering in diamond crystal. Diamond has the space group (Fd3m) and many other crystals of the sodium chloride (Fm3m) , cesium chloride (Pm3m), cesium fluoride (Fm3m) and perovskite (Pm3m) types have the highest symmetry m3m of all known centrosymmetric crystals and it is to be regretted that, expect LiF [3] , they have not as yet been used for SHG in transmission. Crystals like those, and ones belonging to other centrosymmetric classes especially mmm, 4/mmm, 6/mmm, $\bar{3}$m should be tested for SHG in the free fieldless state and for induced SHG in electric and magnetic fields. In the latter case, a particularly interesting situation arises from Eqs (11) and (14) consisting in the simulataneous coupling between the self-induced light intensity dependent effect and DC field effect lowering the crystal symmetry. These optico-electric and optico-magnetic coupling effects are especially large in statistically inhomogeneous bodies, where reorientation of asymmetric microelements can occur. As is seen from Eqs (15) and (16), studies of SHG amplification in appropriately selected centrosymmetric crystals by the method of crossed fields $\underline{E}^{0}$ and $\underline{B}^{0}$ can also prove of interest.

Obviously, examples of SHG phase matching conditions would have exceeded the limits of this paper. We primarily hoped to stimulate interest in more intense, experimental studies of the structure of centrosymmetric crystals by the methods of SHG.

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