Optical nonlinear fourth- and fifth-order susceptibilities

V. I. Zavelishko, V. A. Martynov, S. M. Saltiel, and V. G. Tunkin

M. V. Lomonosov State University, Moscow

(Submitted June 14, 1975)

Kvant. Elektron. (Mosc.) 2, 2541–2544 (November 1975)

An analysis was made of the optical nonlinear susceptibilities responsible for nonlinear effects of the fourth and fifth order in respect of the electromagnetic field. The corresponding fifth- and sixth-rank tensors are obtained for all crystallographic classes and for the isotropic case. The results are tabulated.

PACS numbers: 42.65.−k

1. We shall find all nonzero components of the fifth- and sixth-rank nonlinear susceptibility tensors responsible for various five- and six-photon processes in transparent media. These components are calculated on the assumption of complete internal symmetry of the tensors for all crystallographic classes and for an isotropic medium.

2. When a sufficiently strong electromagnetic wave travels across a nonlinear medium, the polarization of the medium depends nonlinearly on the field and can be described by

$$P_i=P_{si}+\chi^{(1)}_{ij}E_j+\chi^{(2)}_{ijk}E_jE_k+\chi^{(3)}_{ijkl}E_jE_kE_l+\chi^{(4)}_{ijklm}E_jE_kE_lE_m+\chi^{(5)}_{ijklmn}E_jE_kE_lE_mE_n+\dots, \quad (1)$$

where $\mathbf{P}_s$ is the spontaneous polarization in the absence of an external field; $\chi^{(1)}$ is the linear susceptibility tensor; $\chi^{(f)}$ are the nonlinear susceptibility tensors of rank $f+1$ ($f=2, \dots 5$); i, j, k, l, m, n assume the values x, y, and z.

The tensor components $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$ and the effects associated with them are considered in a review of Kielich.[1] More recent papers have reported theoretical and experimental investigations of nonlinear processes of higher orders described by the tensors $\chi^{(4)}$ and $\chi^{(5)}$. Lukasik and Ducuing[2] studied experimentally the coherent anharmonic Raman scattering described by the tensor $\chi^{(5)}$. The tensor $\chi^{(4)}$ describes generation of the fourth optical harmonic observed in Ref. 3. Other workers[4] studied theoretically the generation of fourth harmonics. Optical harmonics due to higher nonlinear processes were considered theoretically by Harris.[5]

The present authors are not aware of any investigations of the nonlinear optical susceptibility tensors of rank 5 and 6. Koptsik[6] considers in his book a fifth-rank tensor describing the second-order piezoelectric effect with an internal symmetry $D[[D^2]^2]$, i.e., the first index is fixed and the other two pairs of indices can be transposed, and also the indices within each pair can be transposed (this notation for the internal symmetry is used in Ref. 6). A fifth-rank tensor describing the tertiary electrooptic effect, $[D^2][D^3]$, is discussed in Ref. 7. A sixth-rank tensor, applied to the third-order elasticity with an internal symmetry $[[D^2]^3]$, is considered in Refs. 8–11.

The nonlinear susceptibility tensors describing, for example, optical harmonic generation have different internal symmetries. If the frequencies of all the interacting waves are in the transparency band, the nonlinear susceptibility tensor becomes completely symmetric: $[D^n]$, i.e., transposition of all the indices of the tensor components is permissible.[12]

3. We shall allow for the internal symmetry of the nonlinear susceptibility tensors, and, for simplicity, we shall label their components by two indices: χ_{kl}. The index k is equal to the number of x's and the index l to the number of y's. The number of z's is then $n-k-l$, where n is the rank of the tensor in question:

$$\chi^{(n-1)}_{kl}=\chi^{(n-1)}_{\underbrace{x\dots x}_{k}\underbrace{y\dots y}_{l}\underbrace{z\dots z}_{n-k-l}}. \quad (2)$$

The nonzero components and the number I of independent components of the tensor $\chi^{(4)}$ are given in Table 1; the corresponding information on the tensor $\chi^{(5)}$ is given in Table 2. These tables give only the indices of the components. More complex relationships between the components are denoted by lower-case letters; the meaning of these letters is as follows:

a $\chi_{22}={}^1/_3\chi_{40}$
b $\chi_{41}=-{}^3/_5\chi_{05}$
c $\chi_{32}=-{}^1/_5\chi_{50}$
d $\chi_{23}=-{}^1/_5\chi_{05}$
e $\chi_{14}=-{}^3/_5\chi_{50}$
f $\chi_{20}=\chi_{02}=\chi_{40}=\chi_{04}=\chi_{42}=\chi_{24}={}^1/_5\chi_{00}$
g $\chi_{22}={}^1/_{15}\chi_{00}$
h $\chi_{24}={}^3/_5\chi_{60}-{}^2/_5\chi_{06}$
i $\chi_{42}={}^3/_5\chi_{06}-{}^2/_5\chi_{60}$

TABLE 1. Nonzero components and numbers I of independent components of fourth-order nonlinear susceptibility tensor.

Class	1	2	m	222	$mm2$	4	$\bar{4}$	422	$4mm$	$\bar{4}2m$	3	32	$3m$	6	$\bar{6}$	622	$6mm$	$\bar{6}m2$	23	432	$\bar{4}3m$
I	21	9	12	3	6	5	4	1	4	2	7	2	5	3	4	0	3	2	1	0	1
00	00	00	—	—	00	00	—	—	00	—	00	—	00	00	—	—	00	—	—	—	—
10	10	—	10	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
01	01	—	01	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
20	20	20	—	—	20	20	20	—	20	—	20	—	20	20	—	—	20	—	—	—	—
11	11	11	—	11	—	—	11	—	—	11	—	—	—	—	—	—	—	—	11	—	11
02	02	02	—	—	02	20	−20	—	20	—	20	—	20	20	—	—	20	—	—	—	—
30	30	—	30	—	—	—	—	—	—	—	30	30	—	—	30	—	—	—	—	—	—
21	21	—	21	—	—	—	—	—	—	—	−03	—	−03	—	−03	—	—	−03	—	—	—
12	12	—	12	—	—	—	—	—	—	—	−30	−30	—	—	−30	—	—	—	—	—	—
03	03	—	03	—	—	—	—	—	—	—	03	—	03	—	03	—	—	03	—	—	—
A																					A
40	40	40	—	—	40	40	40	—	40	—	40	—	40	40	—	—	40	—	—	—	—
31	31	31	—	31	—	31	31	31	—	31	—	—	—	—	—	—	—	—	11	—	11
22	22	22	—	—	22	22	—	—	22	—	a	—	a	a	—	—	a	—	—	—	—
13	13	13	—	13	—	−31	31	−31	—	31	—	—	—	—	—	—	—	—	11	—	11
04	04	04	—	—	04	40	−40	—	40	—	40	—	40	40	—	—	40	—	—	—	—
50	50	—	50	—	—	—	—	—	—	—	50	50	—	—	50	—	—	—	—	—	—
41	41	—	41	—	—	—	—	—	—	—	b	—	b	—	b	—	—	b	—	—	—
32	32	—	32	—	—	—	—	—	—	—	c	c	—	—	c	—	—	—	—	—	—
23	23	—	23	—	—	—	—	—	—	—	d	—	d	—	d	—	—	d	—	—	—
14	14	—	14	—	—	—	—	—	—	—	e	e	—	—	e	—	—	—	—	—	—
05	05	—	05	—	—	—	—	—	—	—	05	—	05	—	05	—	—	05	—	—	—

TABLE 2. Nonzero components and numbers I of independent components of fifth-order nonlinear susceptibility tensor.

Class	$1, \bar{1}$	$2, m, 2/m$	$222, mm2, mmm$	$4, \bar{4}, 4/m$	$422, 4mm, \bar{4}2m, 4/mmm$	$3, \bar{3}$	$3m, \bar{3}m, 32$	$6, \bar{6}, 6/m$	$622, 6mm, \bar{6}m2, 6/mmm$	$23, m3$	$432, \bar{4}3m, m3m$	Isotropic medium
I	28	16	10	8	6	10	7	6	5	4	3	1
00	00	00	00	00	00	00	00	00	00	00	00	00
10	10	—	—	—	—	—	—	—	—	—	—	—
01	01	—	—	—	—	—	—	—	—	—	—	—
20	20	20	20	20	20	20	20	20	20	20	20	f
11	11	11	—	—	—	—	—	—	—	—	—	—
02	02	02	02	20	20	20	20	20	20	02	20	f
C												C
30	30	—	—	—	—	30	—	—	—	—	—	—
21	21	—	—	—	—	−03	−03	—	—	—	—	—
12	12	—	—	—	—	−30	—	—	—	—	—	—
03	03	—	—	—	—	03	03	—	—	—	—	—
40	40	40	40	40	40	40	40	40	40	02	20	f
31	31	31	—	31	—	—	—	—	—	—	—	—
22	22	22	22	22	22	a	a	a	a	22	22	g
13	13	13	—	−31	—	—	—	—	—	—	—	—
04	04	04	04	40	40	40	40	40	40	20	20	f
B												B
50	50	—	—	—	—	50	—	—	—	—	—	—
41	41	—	—	—	—	b	b	—	—	—	—	—
32	32	—	—	—	—	$\bar{c}$	—	—	—	—	—	—
23	23	—	—	—	—	d	d	—	—	—	—	—
14	14	—	—	—	—	$\bar{e}$	—	—	—	—	—	—
05	05	—	—	—	—	05	05	—	—	—	—	—
60	60	60	60	60	60	60	60	60	60	00	00	00
51	51	51	—	51	—	51	—	51	—	—	—	—
42	42	42	42	42	42	i	i	i	i	20	20	f
33	33	33	—	—	—	−51	—	−51	—	—	—	—
24	24	24	24	42	42	h	h	h	h	02	20	f
15	15	15	—	51	—	51	—	51	—	—	—	—
06	06	06	06	60	60	06	06	06	06	00	00	00

The crystallographic axes of class 2 are selected in such a way that the second-order rotation axis is parallel to the Z axis, whereas for class m the reflection plane is perpendicular to the Z axis. The number of independent components of $\chi^{(4)}$ and $\chi^{(5)}$ agrees, for all classes, with those calculated in Ref. 13.

The adopted notation allows us to use these tables in finding nonzero components and the relationships between them in the case of nonlinear susceptibility tensors of lower ranks for all crystallographic systems except the cubic system and the isotropic case. The components of the tensor $\chi^{(2)}$ are given in Table 1 above the AA line; the components of the tensor $\chi^{(3)}$ are given in Table 2 above the BB line. The components of the tensor $\chi^{(1)}$, describing the linear susceptibility, are also included in Table 2 (above the CC line).

The authors are grateful to S. A. Akhmanov and V. A. Koptsik for valuable discussions and helpful comments.

[1] S. Kielich, Ferroelectrics **4**, 257 (1973).
[2] J. Lukasik and J. Ducuing, Phys. Rev. Lett. **28**, 1155 (1972).
[3] S. A. Akhmanov, A. N. Dubovik, S. M. Saltiel, I. V. Tomov, and V. G. Tunkin, ZhETF Pis'ma Red. **20**, 264 (1974) [JETP Lett. **20**, 117 (1974)].
[4] R. F. Begley, R. L. Byer, D. Chemla, M. M. Choy, R. L. Hervst, R. S. Feigelson, and S. Ciraci, Development of Chalcopyrite Crystals for Nonlinear Optical Applications, Tech. Report, Stanford University, Stanford, Calif. (December 1974).
[5] S. E. Harris, Phys. Rev. Lett. **31**, 341 (1973).
[6] V. A. Koptsik, Shubnikov Groups [in Russian], Moscow State University (1966), p. 67.
[7] O. G. Vlokh and T. T. Lyubitskii, Visn. L'viv. Derzh. Univ. Ser. Fiz., No. 6(14), 3, 105 (1971).
[8] F. G. Fumi, Phys. Rev. **83**, 1274 (1951).
[9] F. G. Fumi, Phys. Rev. **86**, 561 (1952).
[10] R. F. S. Hearmon, Acta Crystallogr. **6**, 331 (1953).
[11] K. Brugger, J. Appl. Phys. **36**, 759 (1965).
[12] D. A. Kleinman, Phys. Rev. **128**, 1761 (1962).
[13] Yu. I. Sirotin, Kristallografiya **5**, 171 (1960) [Sov. Phys.-Crystallogr. **5**, 157 (1960)].

Translated by J. W. Brown

Nonlinear optical properties of molecular crystals of meta-tolylenediamine

V. D. Shigorin, G. P. Shipulo, S. S. Grazhulene, L. A. Musikhin, and V. Sh. Shekhtman

P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow and Institute of Solid-State Physics, Academy of Sciences of the USSR, Moscow

(Submitted June 20, 1975)

Kvant. Elektron. (Mosc.) 2, 2544–2547 (November 1975)

An investigation was made of the absorption spectra of polarized light, dispersion of principal refractive indices, and collinear phase matching in the generation of the second harmonic of $\lambda = 1.06\ \mu$ laser radiation in molecular crystals of meta-tolylenediamine. The relative values of all the independent components of the quadratic susceptibility tensor were determined for these crystals and the value of the second-harmonic conversion coefficient was found. It was concluded that meta-tolylenediamine crystals were promising frequency doublers.

PACS numbers: 42.65.−k, 78.20.Dj

Studies of the nonlinear optical properties of molecular crystals of organic compounds have been particularly concerned with substances composed of the simplest molecules, such as benzene derivatives, because then it is much easier to correlate the optical nonlinearities with the molecular and crystalline structure. The quadratic susceptibilities of crystals of four disubstituted[1-3] and two trisubstituted[1] benzene compounds have been determined recently in studies of second harmonic generation. The second harmonic of the $\lambda = 1.06\ \mu$ radiation can also be generated efficiently in powders[4] and single crystals[5] of another trisubstituted