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# Measurement of $\chi^{(2)}$ components by comparing polarization resolved second order cascade processes

G.I. Petrov, S.M. Saltiel, A.B. Ivanova
Sofia University, Faculty of Physics, Department QE, 5 James Bourchier blv, 1264 Sofia, Bulgaria

**ABSTRACT**

Cascade third harmonic generation proves to be a versatile tool to access $\chi^{(2)}$ tensor components. Wherever cascade third harmonic generation allows an interference between two second order processes it will be able to determine ratio of tensor components. We give a full account for orthorhombic class mm2. Given is a discussion of trigonal classes. Polarization resolved signal of cascade third harmonic generation in LBO crystal has been recorded and analyzed.

Keywords: cascade third harmonic generation, mm2, $LiB_3O_5$, second order nonlinearity

## 1. INTRODUCTION

Measurement of second order susceptibility tensor components is important from one side for the prediction of the efficiency of different types of second order processes in the investigated crystal and from another side for comparison with the values obtained by different calculation models. Measurement of $\chi^{(2)}$ components of single crystal can be done by investigation both phase matched and nonphase matched single second order processes. Using phase matched processes has this advantage that their efficiency is many orders of magnitudes higher that the non-phase matched process and that it is not necessary to be used very high power laser sources (or photon counting systems). The disadvantage of this method is the fact that not all $\chi^{(2)}$ components are involved in the effective second order nonlinearities responsible for single phase matched second order process.

In this paper we show that this disadvantage can be overcome by using phase matched cascade second order processes in single crystal. We demonstrate both theoretically and experimentally that the investigation of phase matched cascade third harmonic generation (CTHG) can be an useful tool for measurement of relative magnitude and sign of all $\chi^{(2)}$ tensor components. Previously CTHG has been investigated in [1,2,3] with the purpose to estimate the value of cubic nonlinearity in noncentrosymmetric crystals. In none of these papers are provided the correct expressions for phase matched third harmonic generation due to cascade second order processes. In the next paragraph we start with the theoretical considerations for the processes of CTHG for all allowed phase matched directions.

## 2.THIRD HARMONIC GENERATION DUE TO CASCADE SECOND ORDER PROCESSES IN SINGLE NONCENTROSYMMETRIC CRYSTAL

Let us consider $\chi^{(2)}$ media with input one fundamental wave $A_1(\omega_1)$. In the media as a result of frequency doubling the generated field $A_2$ at $\omega_2 = 2\omega_1$ and also as a result of the process of sum frequency mixing the field $A_3$ at frequency $\omega_3 = \omega_2 + \omega_1 = 3\omega_1$. The three complex amplitudes are described by the following system of equations (it is assumed nondepletion of the fundamental wave).

$$\frac{dA_1}{dz} = 0 \qquad (1)$$

$$\frac{dA_2}{dz} = -i\sigma_2 A_1^2 \exp(i\Delta k_{SHG} z) \qquad (2)$$

$$\frac{dA_3}{dz} = -i\sigma_2' A_1 A_2 \exp(i\Delta k_{SFG} z) \qquad (3)$$

where $\Delta k_{SHG} = k_2 - 2k_1$, $\Delta k_{SFG} = k_3 - k_2 - k_1$. $\sigma_2$ and $\sigma_2'$ are the coupling coefficients for the second harmonic and the sum frequency mixing processes, that include the convolution of second order susceptibility tensor $d^{(2)}$ with the polarization units vectors $\vec{e}_i$ of the three interacting waves $\sigma_2 = \frac{\omega_2}{cn_2}\langle \vec{e}_2 d^{(2)} : \vec{e}_1 \vec{e}_1 \rangle = \frac{\omega_2}{cn_2} d_{eff,SHG}$; $\sigma_2' = \frac{\omega_3}{cn_3}\langle \vec{e}_3 d^{(2)} : \vec{e}_2 \vec{e}_1 \rangle = \frac{\omega_3}{cn_3} d_{eff,SFG}$. The solution of (2) is:

$$A_2(z) = -i\sigma_2 A_1^2 [\exp(i\Delta k_{SHG} z) - 1] / (i\Delta k_{SHG}) \qquad (4)$$

is substituted in (3) and then integrating it gives for the third harmonic field:

$$A_3(z) = \frac{\sigma_2 \sigma_2' A_1^3}{\Delta k_{SHG}} \left[ \frac{\exp(i(\Delta k_{SHG} + \Delta k_{SFG})z) - 1}{(\Delta k_{SHG} + \Delta k_{SFG})} - \frac{\exp(i\Delta k_{SFG} z) - 1}{\Delta k_{SFG}} \right] \qquad (5)$$

From expression (5) it follows that phase matched cascade third harmonic generation is possible along propagation directions of a birefringent crystal that allow phase matched second harmonic generation (SHG) with $\Delta k_{SHG} \to 0$, sum frequency generation with $\Delta k_{SFG} \to 0$ as well as along directions with phase matched direct third harmonic generation $\Delta k_{THG} = k_3 - 3k_1 \to 0$. Note that the condition $\Delta k_{THG} \to 0$ corresponds to $\Delta k_{SHG} + \Delta k_{SFG} \to 0$. The expressions for the third harmonic field for the first two conditions $\Delta k_{SHG} \to 0$ and $\Delta k_{SFG} \to 0$ can be easily extracted from the following expressions equivalent to (5):

$$A_3(z) = \frac{i\sigma_2 \sigma_2' A_1^3 z}{\Delta k_{SHG} + \Delta k_{SFG}} \left[ \exp\left( i\left( \Delta k_{SFG} + \frac{\Delta k_{SHG}}{2} \right) z \right) \mathrm{sinc}\left( \frac{\Delta k_{SHG} z}{2} \right) - \exp\left( i\frac{\Delta k_{SFG} z}{2} \right) \mathrm{sinc}\left( \frac{\Delta k_{SFG} z}{2} \right) \right] \qquad (6)$$

a) $\Delta k_{SHG} = (k_2 - 2k_1) \to 0$

$$A_3(z) = \frac{i\sigma_2 \sigma_2' A_1^3 z}{\Delta k_{SFG}} \exp\left( i\left( \frac{\Delta k_{SHG}}{2} + \Delta k_{SFG} \right) z \right) \mathrm{sinc}\left( \frac{\Delta k_{SHG} z}{2} \right) \qquad (7)$$

b) $\Delta k_{SFG} = (k_3 - k_1 - k_2) \to 0$

$$A_3(z) = -i\frac{\sigma_2 \sigma_2' A_1^3 z}{\Delta k_{SHG}} \exp\left( i\frac{\Delta k_{SFG} z}{2} \right) \mathrm{sinc}\left( \frac{\Delta k_{SFG} z}{2} \right) \qquad (8)$$

c) the case $\Delta k_{THG} = (\Delta k_{SHG} + \Delta k_{SFG}) \to 0$ is obtained from (5):

$$A_3(z) = -i\frac{\sigma_2 \sigma_2' A_1^3 z}{\Delta k_{SFG}} \exp\left( i\frac{\Delta k_{SHG} + \Delta k_{SFG}}{2} z \right) \mathrm{sinc}\left( \frac{\Delta k_{SHG} + \Delta k_{SFG}}{2} z \right) \qquad (9)$$

We should note that at these condition THG is generated also by direct third harmonic process on direct cubic nonlinearity of the crystal. For this reason the condition $\Delta k_{THG} \to 0$ is not suitable for measuring $\chi^{(2)}$ tensor components.

Formulae (7-9) allow one to define the intensity, phase and the angular width of CTHG at the considered direction. The comparison of the three formulae shows that the efficiencies of third harmonic generation obtained at these three directions are comparable. Generally the effective cubic nonlinearity $\chi^{(3)}_{eff}$ that describes CTHG is a result of the contributions of several pairs of cascade second order processes each of them having own value of phase mismatch of the nonphase matched step of the process.

From (7) and (8) we find that effective cubic nonlinearities responsible for CTHG under $\Delta k_{SHG} \to 0$ and $\Delta k_{SFG} \to 0$ conditions are:

$$\chi^{(3)}_{eff,i} = \frac{\omega_2 d^{(2)}_{eff,SHG,i} . d^{(2)}_{eff,SFG}}{n_2 c \Delta k_{SFG,i}} \qquad (10a)$$

$$\chi^{(3)}_{eff,i} = \frac{\omega_2 d^{(2)}_{eff,SHG} . d^{(2)}_{eff,SFG,i}}{n_2 c \Delta k_{SHG,i}}, \qquad (10b)$$

respectively with a net $\chi^{(3)}_{eff}$ value $\chi^{(3)}_{eff} = \sum_i^n \chi^{(3)}_{eff,i}$ .

The energy conversion efficiency for Gaussian input pulses is found to be:

$$\eta = \frac{1}{\sqrt{3}} \frac{\omega_3^2 l^2 \left|\chi^{(3)}_{eff}\right|^2 I_{10}^2}{n_3 n_{1a} n_{1b} n_{1c} c_0^4 \varepsilon_0^2} F(\beta) \frac{\sin^2(\Delta k l/2)}{(\Delta k l/2)^2}, \qquad (11)$$

where $l$ stands for the crystal length, $\Delta k$ is the wave vector mismatch of the phase matched step of the CTHG, while $F(\beta)$ function defines the polarization dependence of the THG signal, that will be discussed in the next paragraphs.

**Table 1.** Rotational dependence of cascade THG along directions of phase-matched SHG and SFG

| Phase matching | Interaction type | THG resolved | $\boldsymbol{F}(\beta)$ |
|---|---|---|---|
| $\Delta k_{SHG} \to 0$ | $ss \to f$ | $\boldsymbol{f}$ | $\sin^4(\beta)\left[\cos(\beta) + \boldsymbol{a}\sin(\beta)\right]^2$ |
| | | $\boldsymbol{s}$ | $\sin^4(\beta)\left[\sin(\beta) + \boldsymbol{b}\cos(\beta)\right]^2$ |
| | $sf \to f$ | $\boldsymbol{f}$ | $\sin^2(\beta)\cos^2(\beta)\left[\cos(\beta) + \boldsymbol{a}\sin(\beta)\right]^2$ |
| | | $\boldsymbol{s}$ | $\sin^2(\beta)\cos^2(\beta)\left[\sin(\beta) + \boldsymbol{b}\cos(\beta)\right]^2$ |
| $\Delta k_{SFG} \to 0$ | $ss \to f$ | $\boldsymbol{f}$ | $\sin^2(\beta)[\sin^2(\beta) + \boldsymbol{c}\sin(\beta)\cos(\beta) + \boldsymbol{d}\sin^2(\beta)]^2$ |
| | $fs \to f$ | $\boldsymbol{f}$ | $\cos^2(\beta)[\cos^2(\beta) + \boldsymbol{c}\sin(\beta)\cos(\beta) + \boldsymbol{d}\sin^2(\beta)]^2$ |
| | $sf \to f$ | $\boldsymbol{f}$ | $\sin^2(\beta)[\cos^2(\beta) + \boldsymbol{a}\sin(\beta)\cos(\beta) + \boldsymbol{e}\sin^2(\beta)]^2$ |

Generally the $\chi^{(2)}$ tensor form will allow all six types ($oo \to o$, $oo \to e$, $oe \to o$, $oe \to e$, $ee \to o$, $ee \to e$) of effective nonlinearity to be non zero values, although this is hardly the case for higher symmetry classes. These reduce to four types if Kleinman symmetry conditions are assumed. Only types allowed by dispersion can be phase matched. Cascade THG poses no such a limit to THG along phase matchable directions for SHG and SFG of any type. If all six types of effective nonlinearities are possible then we get for the $F(\beta)$ function [1] for THG, resolved along the slow "s" and fast "f" directions, the dependencies from the Table 1. The angle $\beta$ stands for the input polarization direction and is measured from the "f" polarization direction and the $\boldsymbol{a} = \boldsymbol{sff} / \boldsymbol{fff}$, $\boldsymbol{b} = \boldsymbol{sff} / \boldsymbol{ssf}$, $\boldsymbol{c} = \boldsymbol{ssf} / \boldsymbol{sss}$, $\boldsymbol{d} = \boldsymbol{sff} / \boldsymbol{sss}$, $\boldsymbol{e} = \boldsymbol{ssf} / \boldsymbol{fff}$ stand for ratios of effective nonlinearities of two second order processes. Each of these functions will generate a typical pattern, very sensitive to the sign and the value of tensor components. Wave vector mismatch is a part of these ratios and should be accounted for at appropriate wavelengths. Most notable are the SFG cases that will generate a sixfold dependence when the $d$ and $e$ ratios are negative and a fourfold one when positive. They will always couple non-phase matchable components, whatever the type of SFG is, since a prerequisite that $d$ and $e$ ratios are non zero values is that $sss$ or $fff$ effective nonlinear coefficients respectively are non zero. Consecutively listed in the $\Delta k_{SFG} \to 0$ row of Table 1 are types I, II and III SFG that require that phase matching is achieved between a fast third harmonic wave and two slow pump waves (type I) or a fast low frequency and a slow high frequency pump waves (type II), or vice versa - a slow low frequency and a fast high frequency pump waves (type III).

## 3. ORTHORHOMBIC CLASS mm2

As has been made clear in [4], in a plea for standardization for orthorhombic class mm2, only those tensors be used, that preserve the right handiness of both systems - crystallographic and optical frame. The $c$ crystallographic axis is reserved for the polar twofold axis of the crystal, the shorter of the two nonpolar axis should be assigned $a$, the longer $b$. Then one will have two possible cases $n_x<n_y<n_z$ and $n_x>n_y>n_z$ and three possible assignments of crystallographic to optical frame axis. It has been pointed out as well that as far as mm2 point group symmetry is concerned the interchange of notations of $a$ with $b$ or $x$ with $y$ will lead to the interchange of $d_{32}$ with $d_{31}$ and $d_{24}$ with $d_{15}$ and vice versa of the tensor forms in the optical frame in respect to the assignment that does not preservers the right handedness of one of the reporting frames. There is a persisting controversy in the literature on this topic (compare for instance notations in [5-8] with [4] and [9]. With this in mind we here reproduce the table of effective nonlinear coefficients for all three wave interactions in the principal planes of a crystal of point group mm2 [5] with added interactions that can not be phase matchable at all. These include interactions of the type $ff \to f$ and $ss \to s$. Table 2 is written down for the case that $n_x<n_y<n_z$ and shadowed are interactions that are phase matchable in the respective planes. This table can be easily

**Table2.** Effective nonlinear coefficients for all types of three wave interactions in the principal planes for crystals of point group mm2 with different assignments of the optical to crystallographic frames. Assumed is that $n_x<n_y<n_z$.

| Assignment | Interaction | xy plane | yz plane | xz plane |
|---|---|---|---|---|
| $x,y,z \to a,b,c$ | $oo \to o$ | $d_{33}$ | 0 | 0 |
| | $oo \to e$ | 0 | $d_{31}\sin\theta$ | $d_{32}\sin\theta$ |
| | $oe \to o$ | 0 | $d_{15}\sin\theta$ | $d_{24}\sin\theta$ |
| | $oe \to e$ | $d_{15}\sin^2\varphi + d_{24}\cos^2\varphi$ | 0 | 0 |
| | $ee \to o$ | $d_{31}\sin^2\varphi + d_{32}\cos^2\varphi$ | 0 | 0 |
| | $ee \to e$ | 0 | $(2d_{24}+d_{32})\sin\theta\cos^2\theta + d_{33}\sin^3\theta$ | $(2d_{15}+d_{31})\sin\theta\cos^2\theta + d_{33}\sin^3\theta$ |
| $x,y,z \to b,c,a$ | $oo \to o$ | 0 | 0 | $d_{33}$ |
| | $oo \to e$ | $d_{31}\cos\varphi$ | $d_{32}\cos\theta$ | 0 |
| | $oe \to o$ | $d_{15}\cos\varphi$ | $d_{24}\cos\varphi$ | 0 |
| | $oe \to e$ | 0 | 0 | $d_{24}\cos^2\theta + d_{15}\sin^2\theta$ |
| | $ee \to o$ | 0 | 0 | $d_{32}\cos^2\theta + d_{31}\sin^2\theta$ |
| | $ee \to e$ | $(2d_{24}+d_{32})\cos\varphi\sin^2\varphi + d_{33}\cos^3\varphi$ | $(2d_{15}+d_{31})\cos\theta\sin^2\theta + d_{33}\cos^3\theta$ | 0 |
| $x,y,z \to c,a,b$ | $oo \to o$ | 0 | $d_{33}$ | 0 |
| | $oo \to e$ | $d_{32}\sin\varphi$ | 0 | $d_{31}\cos\theta$ |
| | $oe \to o$ | $d_{24}\sin\varphi$ | 0 | $d_{15}\cos\theta$ |
| | $oe \to e$ | 0 | $d_{15}\cos^2\theta + d_{24}\sin^2\theta$ | 0 |
| | $ee \to o$ | 0 | $d_{31}\cos^2\theta + d_{32}\sin^2\theta$ | 0 |
| | $ee \to e$ | $(2d_{15}+d_{31})\sin\varphi\cos^2\varphi + d_{33}\sin^3\varphi$ | 0 | $(2d_{24}+d_{32})\cos\theta\sin^2\theta + d_{33}\cos^3\theta$ |

rewritten for the case that $n_x > n_y > n_z$. This will not change the interaction types but one should consider that for instance the $xy$ plane will be a "positive" one and phase matchable will be type II/III interactions. Similarly the $yz$ plane will be a "negative" one, while the $xz$ plane for $\theta < \theta_m$ will be a "positive' one and for $\theta > \theta_m$ will be a " negative" one. However, as can be seen from the table this will only change the type of interaction that can be phase matched in the respective plane. The interchange of possible type of phase matching from type I to type II and vice versa with the change of the order of refractive indices from ascending to descending is true for every one of the principal planes of a crystal with point group of symmetry mm2.

It is straight forward then to write down the $a,b,c,d,e$ coefficients for all the principal planes, provided the crystal is identified as either a $n_x<n_y<n_z$ or $n_z<n_y<n_x$ type since one should take in mind the $o,e$ to $f,s$ equivalence. Looking down at Table 2 in search for $d_{eff} \neq 0$ for $sss$ and $fff$ interactions we are convinced that for the $n_x<n_y<n_z$ assignment this is the $x,y,z \rightarrow a,b,c$ equivalence that has $c=0, d \neq 0$ all over the principal planes except for the $xz$ plane at $\theta < \theta_m$. For the $x,y,z \rightarrow b,c,a$ case $c=0, d=0$ everywhere else except for the $yz$ plane and the $x,z$ plane at $\theta < \theta_m$. The assignment $x,y,z \rightarrow c,a,b$ will give a nonzero value of the $d$ parameter only in the $xz$ plane for $\theta > \theta_m$. Table 3 gives the $a,b,c,d,e$ for all possible cases of optical frame to crystallographic system assignments. It is evident from this table that for all crystals of point group of symmetry mm2 there will be no interference between two $\chi^{(2)}$ processes in a polarization resolved cascade THG along directions of SHG of both types. Next by comparison of the nonzero values of the $\boldsymbol{d}$ and $\boldsymbol{e}$ parameters with the type of phase matching in the principal planes, one is convinced that interference between two second order interactions will be possible only for type II and type III SFG directions in the crystal irrespective of the optical frame assignment. Most fruitful will be the cases that allow the largest number of nonzero $\boldsymbol{d}$ parameters in the principal planes, since type II is a more likely process to be allowed by dispersion rather than type III SFG. These are the upper left and lower right corners of Table 3.

**Table 3.** Values of a,b,c,d,e parameters for mm2 point group

| Assignment | $n_x<n_y<n_z$ | | | | | $n_z<n_y<n_x$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $x,y,z \rightarrow a,b,c$ | **a** | **b** | **c** | **d** | **e** | **a** | **b** | **c** | **d** | **e** |
| xy plane | 0 | 0 | 0 | **x** | 0 | 0 | 0 | 0 | 0 | **x** |
| yz plane | 0 | 0 | 0 | **x** | 0 | 0 | 0 | 0 | 0 | **x** |
| xz $\theta<\theta_m$ | 0 | 0 | 0 | 0 | **x** | 0 | 0 | 0 | **x** | 0 |
| xz $\theta>\theta_m$ | 0 | 0 | 0 | **x** | 0 | 0 | 0 | 0 | 0 | **x** |
| $x,y,z \rightarrow b,c,a$ | **a** | **b** | **c** | **d** | **e** | **a** | **b** | **c** | **d** | **e** |
| xy plane | 0 | 0 | 0 | 0 | **x** | 0 | 0 | 0 | **x** | 0 |
| yz plane | 0 | 0 | 0 | **x** | 0 | 0 | 0 | 0 | 0 | **x** |
| xz $\theta<\theta_m$ | 0 | 0 | 0 | **x** | 0 | 0 | 0 | 0 | 0 | **x** |
| xz $\theta>\theta_m$ | 0 | 0 | 0 | 0 | **x** | 0 | 0 | 0 | **x** | 0 |
| $x,y,z \rightarrow c,a,b$ | **a** | **b** | **c** | **d** | **e** | **a** | **b** | **c** | **d** | **e** |
| xy plane | 0 | 0 | 0 | 0 | **x** | 0 | 0 | 0 | **x** | 0 |
| yz plane | 0 | 0 | 0 | 0 | **x** | 0 | 0 | 0 | **x** | 0 |
| xz $\theta<\theta_m$ | 0 | 0 | 0 | 0 | **x** | 0 | 0 | 0 | **x** | 0 |
| xz $\theta>\theta_m$ | 0 | 0 | 0 | **x** | 0 | 0 | 0 | 0 | 0 | **x** |

We have verified all these considerations by observing the polarization dependence of cascade THG along phase matchable directions for SHG and SFG at 1.064 $\mu m$ in $LiB_3O_5$. Everywhere downwards we use the $x,y,z \rightarrow b,c,a$ optical frame to crystallographic system equivalence for reasons that have already been discussed. Note that this is the area with the bold frame in Table 3. The samples used were two 1 mm slabs cut at $\theta = 90^o, \varphi = 0^o$ for type I SHG and at $\theta = 20^o, \varphi = 90^o$ for type II SHG, as well as a 5 mm crystal cut at $\theta = 43^o, \varphi = 90^o$ for type II SFG. As a pump source we use a cw Q-switched and mode-locked laser strictly plane polarized by an intracavity polarizing mirror set at a Brewster angle. Intracavity second harmonic generation arising from the crystalline quartz material of the Q-switch and mode-locker is filtered out by a color glass. Input polarization is rotated by a $\lambda/2$ wave plate and the output signal is analyzed with a quartz Glan prism. Second harmonic and third harmonic signals are detected after appropriate filtering by a color glass filter, analyzed with a monochromator equipped with a photomultiplier. The signal is fed to one channel of a ratiometer, the other one being used for the reference source. Detected signal is normalized to a phase matched SHG or THG respectively to account for intensity fluctuations of the laser.

Fig.1 represents the signals of SHG and THG along $\theta = 43^o, \varphi = 90^o$ that is the phase matchable direction for type II SFG in the $yz$ plane of the crystal. The "fast" or (in this case) the "o" polarized SHG is a fourfold signal over a full input polarization rotation of $2\pi$ radians as for type II interaction. The "slow" or "e" polarized SHG signal has a large maximum when input light polarization is set to coincide with the "e" eigenmode of material's polarization and a small one when light is polarized perpendicular to the $yz$ plane (in this case "o" polarized). Table 2 then gives us that there are two second order processes that contribute to the "slow" or "e" polarized SHG: these are $1\boldsymbol{e}1\boldsymbol{e} \to 2\boldsymbol{e}$ and $1\boldsymbol{o}1\boldsymbol{o} \to 2\boldsymbol{e}$. It is then the "e" polarized SHG signal that gives rise to synchronously generated third harmonic via a phase matched process $1\boldsymbol{o}2\boldsymbol{e} \to 3\boldsymbol{o}$. Tables 1 and 2 can then be used to calculate the form of the $\boldsymbol{d}$ parameter with added wavelength mismatch for $1\boldsymbol{e}1\boldsymbol{e} \to 2\boldsymbol{e}$ and $1\boldsymbol{o}1\boldsymbol{o} \to 2\boldsymbol{e}$ processes as evident from (10b). Walk-off angles $\alpha_2$ and $\alpha_3$ are less than 0.5 degrees [6] and are not accounted for. So in this case:

$$d = \frac{d_{32}\cos\theta}{3d_{31}\sin^2\theta\cos\theta + d_{33}\cos^3\theta}\frac{\Delta k_{1e1e2e}}{\Delta k_{1o1o2e}}$$

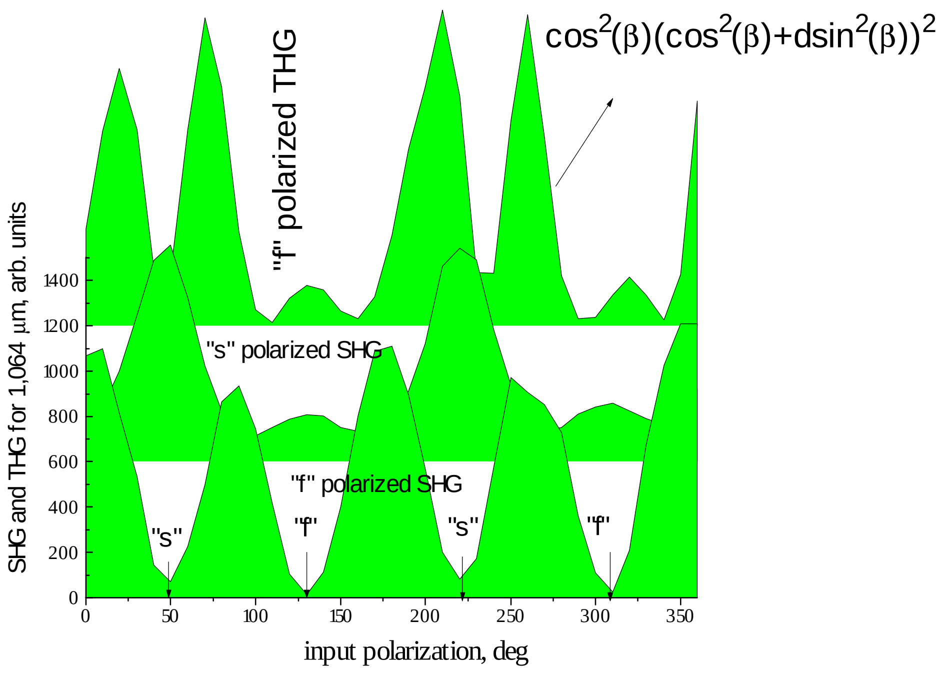


**Fig.1** Polarization resolved SHG and cascade THG signal along type II SFG direction in the yz plane of LBO at a pump wavelength of 1.064 $\mu m$. We note that if assignment is that the shorter of two nonpolar axis is $a$, the other being $b$, the yz plane will be the $ca$ crystallographic plane. This preserves the right handedness of both systems while retaining the accepted order of $n_x<n_y<n_z$. Arrows indicate input polarization coincidence with the slow "e" and fast "o" eigemodes, the equivalence that defines the crystal as a "positive" one in this plane.

We calculate $\Delta k_{1o1o2e} = 5751 cm^{-1}$ and $\Delta k_{1e1e2e} = 1908 cm^{-1}$ with the dispersion relations given by Kato [7]. The approximation to the experimental data then yields that

$$\frac{1.4d_{31} + 0.5d_{33}}{d_{32}} = -1.47 \pm 10\% \qquad (12)$$

In (12) if we neglect the term $0.5d_{33}$ (it is known [9] that $d_{33}$ is less than 6% from $d_{31}$) we obtain $d_{31}/d_{32} = -1.05$; that is in excellent agreement with the published ratios of these two components [8,9]. This way we demonstrate that the proposed by us new method for $\chi^{(2)}$ components measurements can yield correct values for the relative magnitude and sign of different tensor components.

Third harmonic generation can be observed as well along type II SHG (Fig. 2) in the $yz$ plane at $\theta = 20^o, \varphi = 90^o$. The second harmonic signal will be generated via the $1o1e \to 2o$ phase matched process, as well as an "e" polarized second harmonic signal via $1o1o \to 2e$ and $1e1e \to 2e$ processes. However latter two are orders of magnitude weaker than the phase matched process with "o" second harmonic polarization. So third harmonic will be basically generated only due to second harmonic with this polarization. Then possible are just two cases: $2o1o \to 3e$ and $2o1e \to 3o$ with their own angular dependence. As can be seen from Table 2 under Kleinman symmetry conditions the tensor components driving these nonlinear processes are the same. We have compared the signal at the maxima with "3e" and "3o" polarization and verified that this ratio is consistent with the ratio of wave vector mismatch.

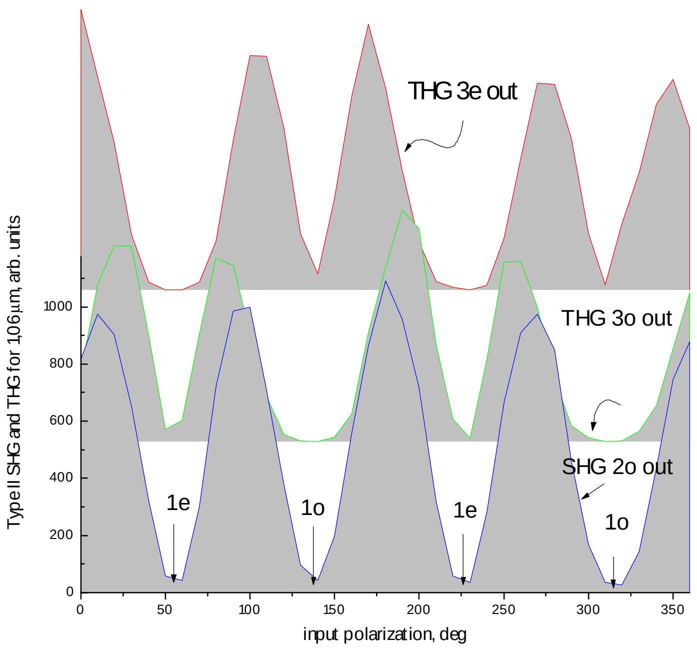


**Fig. 2** SHG and THG along $\theta = 20^o, \varphi = 90^o$, in LBO the direction for type II SHG in the $yz$ plane. Comparison between maximum values with "3e" and "3o" third harmonic signals reveals only the wave vector mismatch of relative processes. Intensity maxima of "3o" THG are displaced by an angle of $arctg(\sqrt{2}/2)$ from the "e" polarization direction. Same is the angular displacement of "3e" THG intensity maxima with respect to "o" polarization direction.

Second harmonic generation at $\theta = 90^o, \varphi = 11^o$ is accomplished by rotation of the $\theta = 90^o, \varphi = 0^o$ slab to the direction that type I $1o1o \to 2e$ SHG appears. Third harmonic is then generated via $2e1e \to 3e$ and $2e1o \to 3o$ processes, each of them being the single contribution to the respective third harmonic polarization. Comparison of maximum values of these rotational dependencies should yield an estimate for the $|d_{31}|/|d_{32} + d_{33}|$ ratio. We found from (10a) and (11) for the ratio of respective third harmonic intensities $I_{3o}/I_{3e}$:

$$\frac{I_{3o}}{I_{3e}} \cong \frac{\left| d_{31}\cos\varphi \sin^3\beta \frac{1}{\Delta k_{1o2e3o}} \right|^2}{\left| \left(3d_{32}\cos\varphi\sin^2\varphi + d_{33}\cos^3\varphi\right)\sin^2\beta\cos\beta \frac{1}{\Delta k_{1e2e3e}} \right|^2}$$

Intensity of measured signals and wave vector mismatches correction ($\Delta k_{1o2e3o} = 6658 cm^{-1}$ and $\Delta k_{1e2e3e} = 4649 cm^{-1}$) then yield the following relation:

$$\frac{\left|0.98 d_{31}\right|}{\left|0.11\left|d_{32}\right| \pm 0.95\left|d_{33}\right|\right|} = 5.65 \pm 10\%, \qquad (13)$$

where the "±" and inner modulus signs in the denominator account for the unknown relative sign of the $d_{33}/d_{32}$ ratio, showing that the sign of the $d_{33}$ component should be the same as the sign of $d_{32}$ if the ratio of $\left|d_{33}\right|/\left|d_{32}\right|$ is close to the published values [8,9]. If we adopt equal signs of $d_{33}$ and $d_{32}$ and measured by us ratio of $d_{31}/d_{32} = -1.05$ we calculate from (13) that $d_{33}/d_{32} = 0.076$, a value close to published magnitudes. We note, however, that measurements done in [8] by the Maker fringe method reveal that the $d_{33}$ component is of the opposite sign of $d_{32}$ and of the sign of $d_{31}$. This discrepancy can be explained by the frequency dispersion of the $\chi^{(2)}$ tensor. We measure $d(3\omega;2\omega,\omega)$ values rather than $d(2\omega;\omega,\omega)$ values accessed at the measurements in [8]. If the sign of the ratio $d_{33}/d_{32} < 0$, then from (13) we obtain $d_{33}/d_{32} = -0.31$.

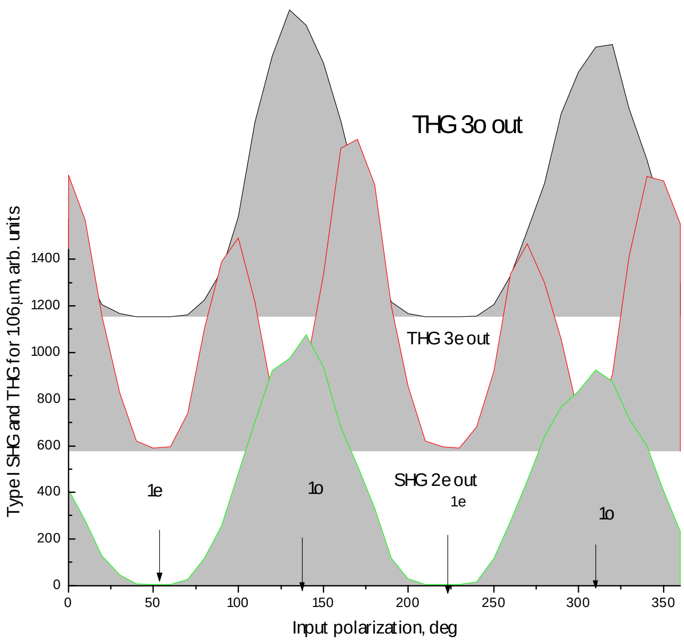


**Fig. 3** SHG and THG along $\theta = 90^o, \varphi = 11^o$. Cascade third harmonic generation is accomplished with "3e" and "3o" polarizations via single second order processes. It is possible to compare intensities between them to establish a ratio between tensor components. Note that this case, $\Delta k_{SHG} \to 0$, of CTHG determined are ratios of $d(3\omega, 2\omega, \omega)$ tensor components, unlike the case of $\Delta k_{SFG} \to 0$, that allows determination of ratios of $d(2\omega, \omega, \omega)$ tensor components.

## 4. TRIGONAL CLASSES

**Table4**. Values of $d_{eff}$ for symmetry classes 3 and 3m

| p.g.s | Interaction | $d_{eff}$ |
|---|---|---|
| 3m | $oo \to o$ | $-d_{22}\cos 3\varphi$ |
| | $oo \to e$ | $-d_{22}\sin 3\varphi\cos\theta + d_{15}\sin\theta$ |
| | $oe \to o$ | $-d_{22}\sin 3\varphi\cos\theta + d_{15}\sin\theta$ |
| | $oe \to e$ | $d_{22}\cos 3\varphi\cos^2\theta$ |
| | $ee \to o$ | $d_{22}\cos 3\varphi\cos^2\theta$ |
| | $ee \to e$ | $d_{22}\sin 3\varphi\cos^3\theta + d_{33}\sin^3\theta + 3d_{15}\sin\theta\cos^2\theta$ |
| 3 | $oo \to o$ | $-d_{22}\cos 3\varphi - d_{11}\sin 3\varphi$ |
| | $oo \to e$ | $(d_{11}\cos 3\varphi - d_{22}\sin 3\varphi)\cos\theta + d_{15}\sin\theta$ |
| | $oe \to o$ | $(d_{11}\cos 3\varphi - d_{22}\sin 3\varphi)\cos\theta + d_{15}\sin\theta$ |
| | $oe \to e$ | $(d_{11}\sin 3\varphi + d_{22}\cos 3\varphi)\cos^2\theta$ |
| | $ee \to o$ | $(d_{11}\sin 3\varphi + d_{22}\cos 3\varphi)\cos^2\theta$ |
| | $ee \to e$ | $d_{22}\sin 3\varphi\cos^3\theta - d_{11}\cos 3\varphi +$ $+ d_{33}\sin^3\theta + d_{15}\sin 2\theta\cos\theta + d_{31}\cos^2\theta\sin\theta$ |

Looking down at the table of the d-matrix for different symmetry classes, one can be easily convinced that this method will be useful for the trigonal classes where a large enough variety of tensor components is to be determined. We here give as an example in Table 4 the effective nonlinear coefficients for just two of them - point groups 3 and 3m that will allow non zero values of the interactions $ss \to s$ and $ff \to f$, with Kleinman symmetry assumed. Then it is straight forward to obtain the $c$ and $d$ values, these that contribute to the specific polarization dependence of THG along type I and type II SFG directions. We note that these cases are before all phase matchable as determined by dispersion, rather than type III interaction. Table 5 gives the above mentioned values for the case of a negative crystal.

As far as point group 3m is concerned having a crystal cut for type II SFG at $\varphi = 0^o$ the slope of modulation of the sixfold pattern (as set by the always negative value of the $d$ parameter) will give the value of $c = -d_{15}\sin\theta / d_{22}$. We note that the sign of this ratio is an estimate for the optimum $\varphi$ angle that the crystal should be cut for type I interaction ($\varphi = 30^0$ if it is a positive value and $\varphi = 90^0$ if a negative one). With the value of $\mathbf{d_{15}} / \mathbf{d_{22}}$ ratio then one can turn to type II SHG interaction for a crystal cut with optimum $\varphi = 0^0$. The $b$ parameter would not yield any new information but return back the already known $d_{15} / d_{22}$ ratio. However resolving the opposite "$e$" polarized THG signal we will be able to deduce the $d_{33} / d_{22}$ ratio from $1/a = 3\sin\theta d_{15} / d_{22} + tg^2\theta\sin\theta d_{33} / d_{22}$.

**Table 5**. ***c*** and ***d*** values for point group symmetry 3m and 3

| Symmetry | $c$ | $d$ |
|---|---|---|
| 3m | $tg3\varphi\cos\theta - \frac{d_{15}}{d_{22}}\frac{\sin\theta}{\cos 3\varphi}$ | $-\cos^2\theta$ |
| 3 | $\frac{d_{22}\sin 3\varphi - d_{11}\cos 3\varphi}{d_{22}\cos 3\varphi + d_{11}\sin 3\varphi} - \frac{d_{15}\sin\theta}{d_{22}\cos 3\varphi + d_{11}\sin 3\varphi}$ | $-\cos^2\theta$ |

In the same way a crystal of point group of symmetry 3 cut for type I or II SFG direction will always exhibit a sixfold polarization dependence of the cascaded THG. The modulation parameters $c = -d_{11}\cos\theta / d_{22} - d_{15}\sin\theta / d_{22}$ for $\varphi = 0$ and $c = -d_{22}\cos\theta / d_{11} - d_{15}\sin\theta / d_{11}$ for $\varphi = 30^0$ define different slopes of modulation of the pattern over a rotation of the input polarization every 180 degrees. We note that these ratios will determine the sign of the $d_{11} / d_{22}$ ratio although they are not enough to determine the relative values of all $d_{11} / d_{22}$, $d_{15} / d_{22}$, $d_{15} / d_{11}$ ratios. All these values are necessary so that an optimum $\varphi$ angle be calculated for type I and type II interactions that is generally neither $\varphi = 0$ nor $\varphi = 30^0$ in spite of the $3\varphi$ dependence of the respective type of interactions ($oo \to e$ and $oe \to e$).

## 5. CONCLUSION

We show that there are three phase matched conditions in noncentrosymmetrical crystals at which phase matched third harmonic can be generated with comparable efficiency. Comparison the efficiency of the process of THG for $\Delta k_{SHG} \to 0$ and $\Delta k_{SFG} \to 0$ allows determination of the relative magnitude and sign for the components of the $\chi^{(2)}$ tensor of the considered crystal. It is found that for the crystal of $LiB_3O_5$ $d_{31}(2\omega,\omega,\omega) / d_{32}(2\omega,\omega,\omega) = -1.05$ that is in excellent accordance with published results.

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