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Ultrasonic measurement of the elastic properties of benzoyl glycine single crystals

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Abstract. Certain organic crystals are found to possess high non-linear optical coefficients, often one to two orders of magnitude higher than those of the well-known inorganic non-linear optical materials. Benzoyl glycine is one such crystal whose optical second-harmonic generation efficiency is much higher than that of potassium dihydrogen phosphate. Single crystals of benzoyl glycine are grown by solvent evaporation technique using N, N-dimethyl formamide as the solvent. All the nine second-order elastic stiffness constants of this orthorhombic crystal are determined from ultrasonic wave velocity measurements employing the pulse echo overlap technique. The anisotropy of elastic wave propagation in this crystal is demonstrated by plotting the phase velocity, slowness, Young's modulus and linear compressibility surfaces along symmetry planes. The volume compressibility, bulk modulus and relevant Poisson's ratios are also determined. Variation of the diagonal elastic stiffness constants with temperature over a limited range are measured and reported.

Keywords. Benzoyl glycine; non-linear optical crystals; elastic constants; ultrasonic measurements; phase velocity surfaces.

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1. Introduction

The non-linear optical (NLO) properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during the past two decades [1–3]. Organic NLO materials play an important role in second-harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation, optical bi-stability etc. [4]. Recently, a number of organic compounds with non-localized π-electron systems having large dipole moments have been synthesized to realize non-linear susceptibilities far larger than well-known inorganic non-linear optical materials [5,6]. However, their practical applications are rather limited due to poor chemical stability and red shift of the cut-off wavelength, caused by the large organic n-conjugated group. Moreover, the

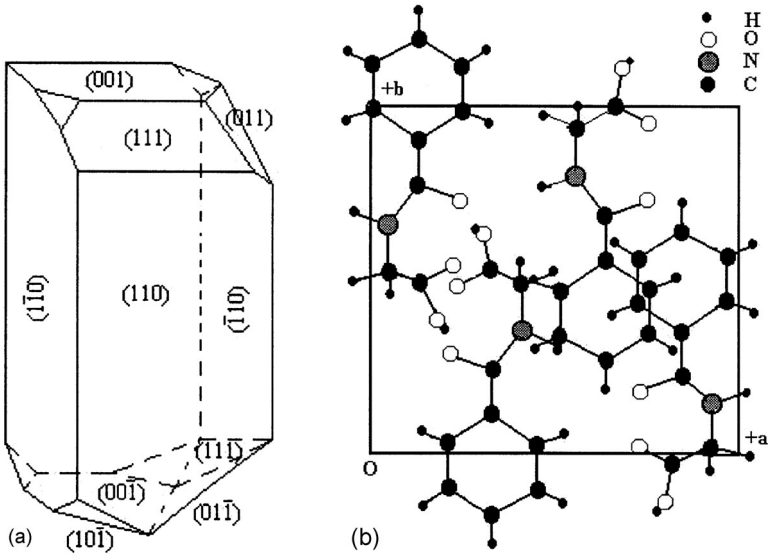

Figure 1. (**a**) Morphology of BG single crystal. (**b**) Molecular packing viewed along the c-axis.

large birefringence resulting from the stacking of the structure radical, and several other factors [7] lead to poor phase matching of optical waves in these materials.

Benzoyl glycine (BG) or hippuric acid with the chemical formula C_6H_5–CONH–CH_2–COOH is reported to be an excellent NLO crystal. The range of optical transparency of benzoyl glycine single crystal is reported to be much larger than other well-characterized organic NLO crystals such as 3-methyl-4-nitropyridine-1-oxide (POM), N-(4-nitrophenyl)-L-prolinol (NPP), vanillin etc. [8]. This indicates its stability for the generation and mixing of frequencies over a wide wavelength range of the electromagnetic spectrum. Second-harmonic generation (SHG) efficiency of benzoyl glycine has been initially tested by Kurtz powder technique [9]. A second harmonic ($\lambda = 532$ nm) output power of 7.7 mW has been reported for an input power of 21 mW using Q switched, mode locked Nd : YAG laser ($\lambda = 1064$ nm) using single crystal samples. The efficiency of SHG is about 37% for this crystal, which is much higher than that of potassium dihydrogen phosphate (22%). Thus this crystal can efficiently be used for up-conversion of IR radiation into visible green light. Benzoyl glycine crystallizes into the orthorhombic structure with space group $P2_12_12_1$ having lattice parameters $a = 9.112$ Å, $b = 10.566$ Å and $c = 8.855$ Å [8]. One of the previously reported crystal lattice parameters, $a = 8.874$ Å, $b = 10.577$ Å and $c = 9.177$ Å [10], are not as per the IRE standards [11]. The melting point of this crystal is reported to be 187°C. It contains no water of crystallization. The morphology of the crystal and the molecular packing as viewed down the c-axis are shown in figures 1a and b respectively.

In this paper we report the elastic properties of BG crystal measured using ultrasonic pulse echo overlap (PEO) technique. All the nine second-order elastic stiffness constants at room temperature, defined as per the recommendations of IRE, along

with related elastic parameters, Poisson's ratios, bulk modulus, Young's modulus and compressibility (linear and volume) are reported. Phase velocity, slowness and linear compressibility surfaces are drawn to bring out anisotropy in the elastic properties of this crystal. Variations of diagonal elastic constants with temperature over a limited range are also given. Details of the experimental techniques used in the work, results obtained and a discussion of the results are given in the following sections.

2. Experimental details

Large single crystals of benzoyl glycine are grown from its supersaturated solution by the slow evaporation technique. N,N-dimethyl formamide is found to be the ideal solvent to grow large single crystals by slow and controlled evaporation. Single crystals of about $70 \times 25 \times 8$ mm^3 size are grown over a period of about five weeks. Morphology of the grown crystals is identified by measuring the interfacial angles with an accurate contact goniometer and comparing with values calculated from crystallographic data. The well-developed planes are identified as (110), (001), (111) and (011). Samples for ultrasonic velocity measurements are cut in the form of rectangular parallelepiped with parallel planes perpendicular to [100], [010], [001], [110], [011] and [101] directions using a slow speed diamond wheel saw. These planes of interest are lightly polished without spoiling the parallelism between pairs of planes. X-cut and Y-cut quartz transducers of 10 MHz resonant frequency are used to generate ultrasonic wave pulses and to detect the successive echoes generated by reflections from the rear end of the sample. Silicon grease is found to be a suitable bonding medium to transmit mechanical vibrations generated by the transducer into the sample. The round trip travel times of ultrasonic wave pulses inside the crystal are measured accurately by the pulse echo overlap (PEO) technique [12]. Details of the various techniques to measure ultrasonic wave velocity in solid samples, including PEO technique, are reviewed by Papadakis [13]. A MATEC model 7700 pulse modulator and receiver system, with its associated sub-units are used for the present measurements.

The McSkimin Δt correction [14,15] is applied to identify the correct cycle-to-cycle overlap of the detected echoes in each measurement, and correct for the additional phase change introduced by the bonding medium. The density of the crystal is measured to be 1284 kg m^{-3}. Twelve velocity measurements along selected symmetry directions in a crystal with orthorhombic symmetry allow one to evaluate all the second-order elastic stiffness constants, with cross checks possible on some of the values. Standard expressions available in literature [16] are used to evaluate the nine elastic constants from velocity data. The accuracy of these measurements is estimated to be better than 0.2% in the case of diagonal elastic constants and is around 1% in the case of off-diagonal elastic constants, considering all sources of errors in the measurements.

The variations of the diagonal elastic constants with temperature are measured by keeping the crystal-transducer assembly in a temperature-controlled oven. Variations in the round trip travel times are recorded for both longitudinal and transverse waves in the temperature range 300–380 K. Thermal expansion of the crystal is neglected while evaluating the temperature variation of wave velocities.

Table 1. Velocities of various ultrasonic modes in benzoyl glycine at room temperature. L, T and QL represent longitudinal, transverse and quasi-longitudinal modes respectively. Relations between elastic constants and respective mode velocities are given in the last column.

Sl. No.	Mode	Direction of propagation	Direction of polarisation	Velocity (m s^{-1})	Relation between mode velocity and elastic constant
1	L	[100]	[100]	$v_1 = 2696 \pm 5$	$C_{11} = \rho v_1^2$
2	L	[010]	[010]	$v_2 = 4235 \pm 8$	$C_{22} = \rho v_2^2$
3	L	[001]	[001]	$v_3 = 3189 \pm 6$	$C_{33} = \rho v_3^2$
4	T	[001]	[010]	$v_4 = 1041 \pm 2$	$C_{44} = \rho v_4^2$
5	T	[010]	[001]	$v_5 = 1033 \pm 2$	$C_{44} = \rho v_5^2$
6	T	[001]	[100]	$v_6 = 1794 \pm 4$	$C_{55} = \rho v_6^2$
7	T	[100]	[001]	$v_7 = 1784 \pm 4$	$C_{55} = \rho v_7^2$
8	T	[100]	[010]	$v_8 = 2291 \pm 5$	$C_{66} = \rho v_8^2$
9	T	[010]	[100]	$v_9 = 2274 \pm 5$	$C_{66} = \rho v_9^2$
10	QL	[110]	QL	$v_{10} = 3852 \pm 8$	$C_{12} = f_{ab}^{a}$
11	QL	[011]	QL	$v_{11} = 2988 \pm 6$	$C_{23} = f_{bc}^{b}$
12	QL	[101]	QL	$v_{12} = 3146 \pm 6$	$C_{13} = f_{ac}^{c}$

[a] $f_{ab} = \{[c^2C_{11} + s^2C_{66} - \rho v_{10}^2][c^2C_{66} + s^2C_{22} - \rho v_{10}^2]/c^2s^2\}^{1/2} - C_{66}$.
[b] $f_{bc} = \{[c^2C_{22} + s^2C_{44} - \rho v_{11}^2][c^2C_{44} + s^2C_{33} - \rho v_{11}^2]/c^2s^2\}^{1/2} - C_{44}$.
[c] $f_{ac} = \{[s^2C_{11} + c^2C_{55} - \rho v_{12}^2][s^2C_{66} + c^2C_{33} - \rho v_{12}^2]/c^2s^2\}^{1/2} - C_{55}$.

Here s and c are the sine and cosine of the angle of rotation with the respective axes. The angles of rotation are measured from a, b and c axis respectively.

Table 2. The elastic modulii and Poisson's ratios of benzoyl glycine at room temperature (300 K).

Elastic stiffness constants (GPa)	Elastic compliance constants ($\times 10^{-10}$ m^2 N^{-1})	Poisson's ratios
$C_{11} = 9.33 \pm 0.02$	$S_{11} = 1.41 \pm 0.01$	
$C_{22} = 23.03 \pm 0.05$	$S_{22} = 0.50 \pm 0.01$	$\nu_{12} = 0.44$
$C_{33} = 13.06 \pm 0.03$	$S_{33} = 1.00 \pm 0.01$	$\nu_{21} = 0.16$
$C_{44} = 1.39 \pm 0.01$	$S_{44} = 7.19 \pm 0.01$	
$C_{55} = 4.13 \pm 0.01$	$S_{55} = 2.42 \pm 0.01$	$\nu_{23} = 0.09$
$C_{66} = 6.74 \pm 0.01$	$S_{66} = 1.48 \pm 0.01$	$\nu_{32} = 0.17$
$C_{12} = 4.95 \pm 0.05$	$S_{12} = -0.22 \pm 0.01$	
$C_{23} = 4.36 \pm 0.04$	$S_{23} = -0.09 \pm 0.01$	$\nu_{13} = 0.46$
$C_{13} = 4.76 \pm 0.05$	$S_{13} = -0.44 \pm 0.01$	$\nu_{31} = 0.31$

3. Results and discussion

Velocities of propagation of longitudinal and transverse ultrasonic waves along selected directions in benzoyl glycine crystal are listed in table 1, along with the relevant expressions relating ultrasonic velocities and elastic constants for an orthorhombic crystal. All the nine second-order elastic stiffness constants, compliance

constants and the respective Poisson's ratios are tabulated in table 2. The volume compressibility [17] of this crystal is calculated to be 1.371 $\times$ 10^{-10} m^2 N^{-1} and the corresponding bulk modulus is 7.29 GPa.

In order to get a clear picture of anisotropy of elastic wave propagation in this crystal, we have plotted the phase velocity, slowness and group velocity surfaces along various symmetry planes. Phase velocity is defined as ω/k whereas group velocity $(\partial\omega/\partial k)$ is the velocity with which the modulation envelope of the wave packet travel in the medium. The dispersion relation for plane acoustic wave in a medium is given by [18]

$$\Omega(\omega, k_x, k_y, k_z) = 0.$$

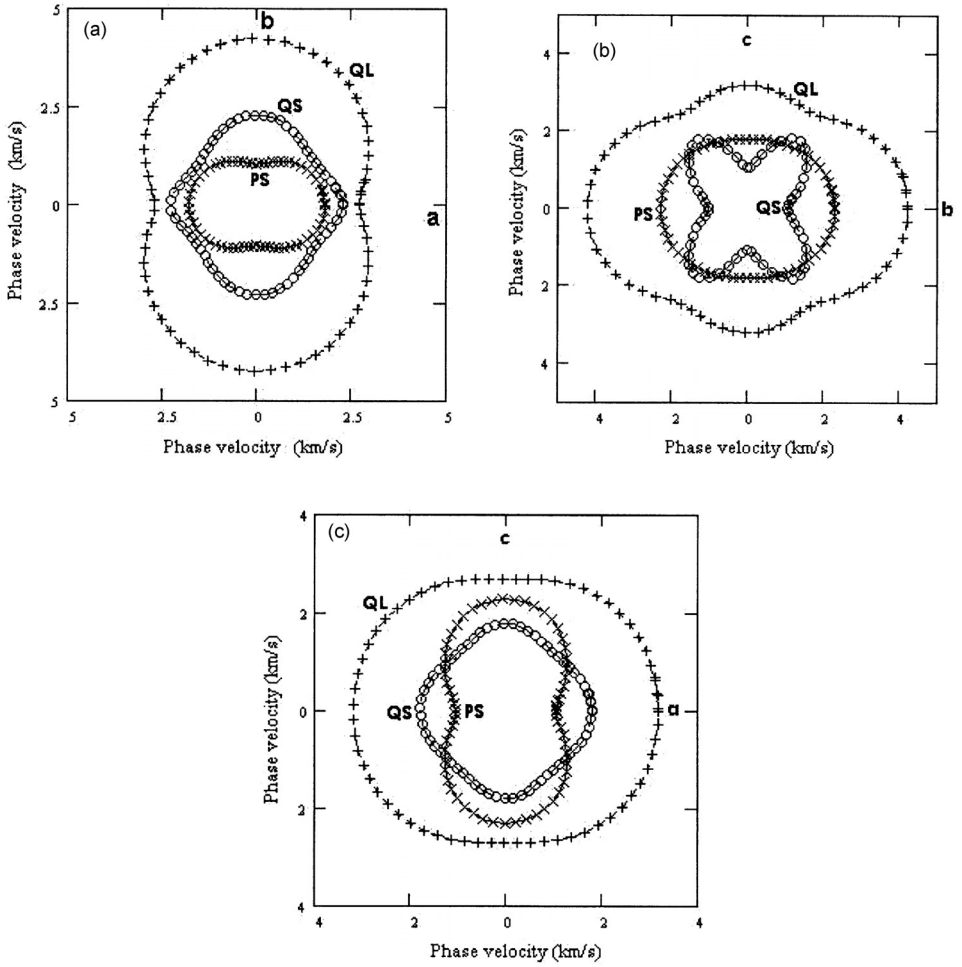

Figure 2. (**a**) Phase velocity surfaces in the a–b plane at 300 K. (**b**) Phase velocity surfaces in the b–c plane at 300 K. (**c**) Phase velocity surfaces in the a–c plane at 300 K.

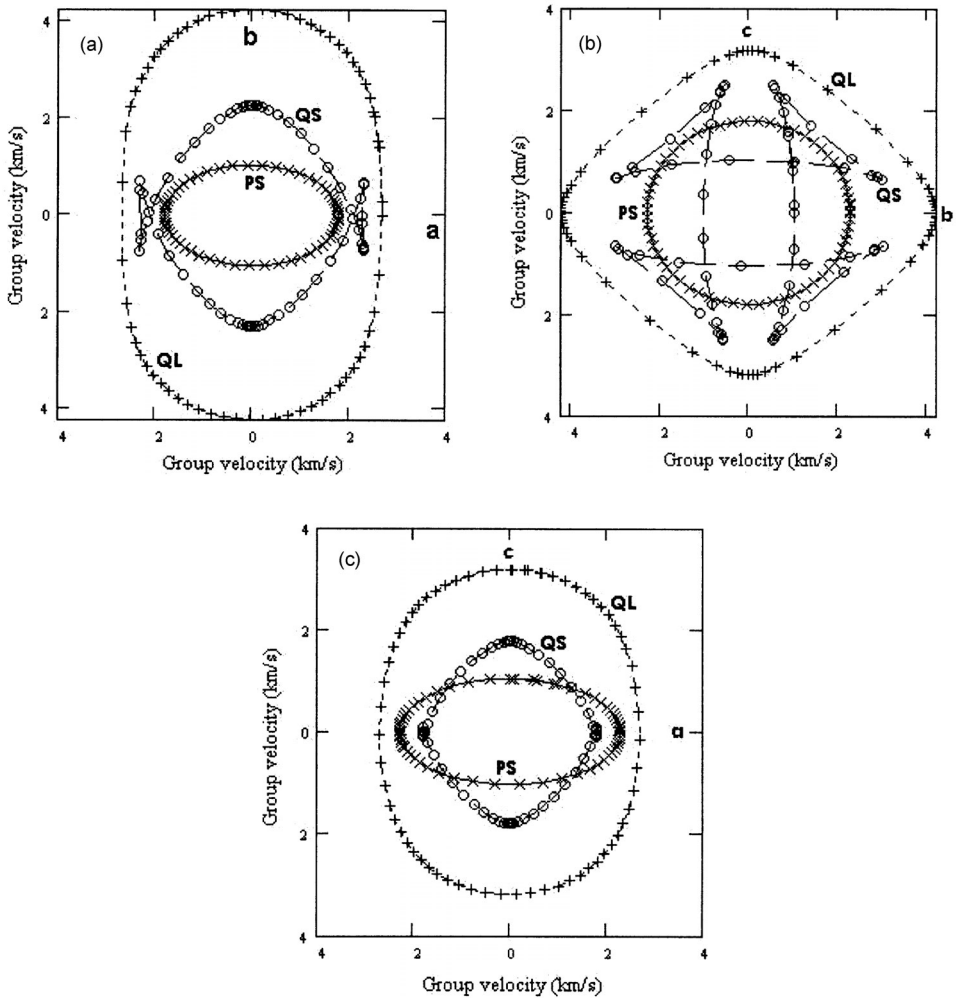

Figure 3. (**a**) Group velocity surfaces in the a–b plane at 300 K. (**b**) Group velocity surfaces in the b–c plane at 300 K. (**c**) Group velocity surfaces in the a–c plane at 300 K.

Implicit differentiation of this relation enables one to evaluate components of group velocity vector along the principal symmetry planes. Relevant expressions to evaluate these components are of the form

$$\left(\frac{\partial\omega}{\partial k_x}\right)_{k_y k_z} = -\left(\frac{\partial\Omega}{\partial k_x}\right) \Big/ \left(\frac{\partial\Omega}{\partial\omega}\right) = \nu_{gx}.$$

Similar expressions hold good for v_{gy} and v_{gz}. Expressions for the components of group velocity have been derived analytically (which include non-zero elastic constants and appropriate direction cosines) and they were computed to obtain the group velocity plots.

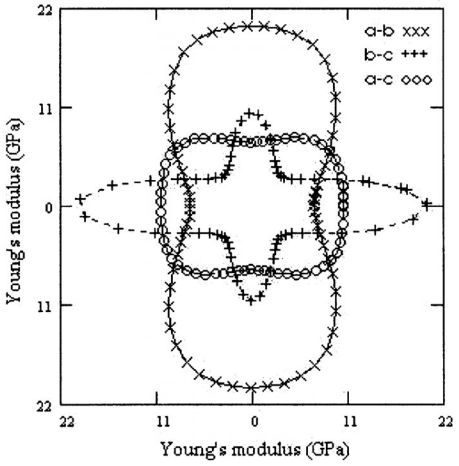

Figure 4. Young's modulus surfaces in the a–b ($\times$ $\times$ $\times$), b–c ($+$ $+$ $+$), and a–c ($\circ$ $\circ$ $\circ$) planes at 300 K.

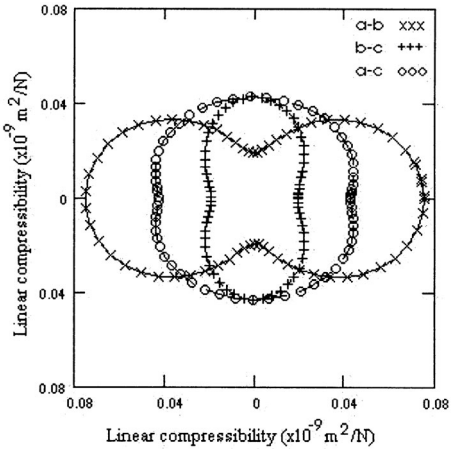

Figure 5. Linear compressibility surfaces in the a–b ($\times$ $\times$ $\times$), b–c ($+$ $+$ $+$), and a–c ($\circ$ $\circ$ $\circ$) planes at 300 K.

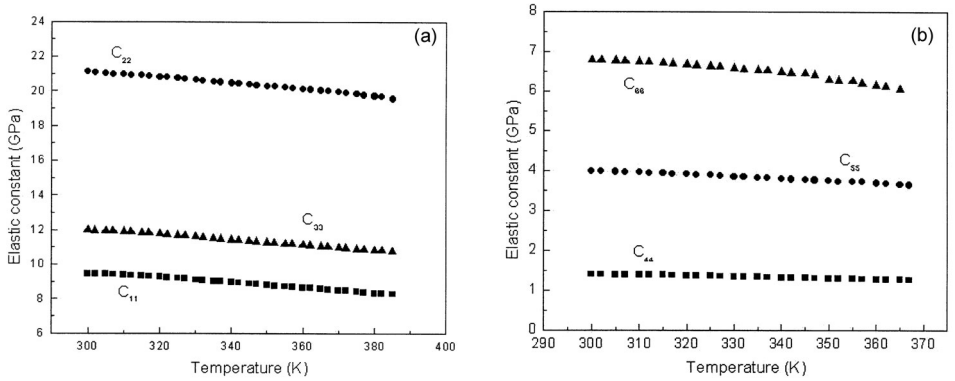

Figure 6. (**a**) Temperature dependence of the elastic constants, C_{11}, C_{22} and C_{33} in BG. (**b**) Temperature dependence of the elastic constants C_{44}, C_{55} and C_{66} in BG.

The phase velocity surfaces for the pure shear, quasi-shear and quasi-longitudinal modes along the a–b, b–c and a–c planes are shown in figures 2a, b and c respectively. Sections of the corresponding group velocity surfaces along the symmetry planes are shown in figures 3a, b and c. It may be noted that wave propagation, particularly the quasi-shear mode, is highly anisotropic in this crystal. The quasi-shear mode exhibits cuspidal edges along symmetry directions in the group velocity surfaces. Along these directions, the phase and group velocities do not have a one-to-one correspondence and they are not collinear. More than one group velocity vector correspond to a phase velocity vector and wave propagation is highly anisotropic in these directions. These features are also reflected in the corresponding slowness surfaces (not shown in the paper).

The Young's modulus and linear compressibility surfaces along different symmetry planes are shown in figures 4 and 5 respectively. These parameters also exhibit considerable anisotropy in their values lying in these planes.

Temperature dependence of the diagonal elastic stiffness constants over a limited temperature range are shown in figures 6a and b. There is a gradual decrease in the values of elastic constants with rise in temperature. These curves do not exhibit any anomaly in this temperature range, indicating the absence of any elastic anomaly or phase transition in this crystal. This crystal is not known to exhibit any phase transition in any temperature range, from any other measurements.

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