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Third Harmonic Generation of Transverse Acoustic Waves in Crystals and Ceramics

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Summary

When transverse acoustic waves propagate in isotropic solids and in some specially orientated crystals the quadratic or the second order nonlinearity does not exist. The third harmonic generation (THG) of transverse waves in such materials is investigated in this paper. Since the quadratic nonlinearity does not exist, the third harmonic wave is generated solely by the cubic nonlinear interactions of the fundamental waves. A nonlinearity parameter for the THG is defined analog to the second harmonic generation of longitudinal waves. This parameter involves the linear combination of the second-, third- and fourth-order elastic constants. If the relevant second- and third-order constants are known, the fourth-order constants can be isolated from the measured nonlinearity parameters. Experiments of third harmonic generation in shear waves are carried out for poled and unpoled PZT4 ceramics. The appropriate nonlinearity parameters are determined, which give some combinations of the second-, third- and fourth-order elastic constants. This THG provides a new way to determine the fourth-order elastic constants of materials in addition to the static pressure measurements.

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1. Introduction

The acoustic harmonic generation in solids has been extensively investigated [1, 2, 3]. In first-order approximation, the harmonic waves are considered to be generated by collinear nonlinear interactions of the acoustic waves. It is known that there are three kinds of acoustic modes for a given wave propagation direction in an anisotropic solids. The different interaction process of those acoustic waves can be used to distinguish the harmonic generation. First, the harmonic wave of one acoustic mode is generated by the nonlinear self-interaction of the same mode. Second, the harmonic wave of one acoustic mode is generated by the nonlinear self-interaction of another mode of acoustic wave. Third, the harmonic wave is generated by the nonlinear cross-interaction of acoustic waves of different modes. Since the velocities of different acoustic modes are usually different (except for the case of degenerate transverse waves), only the first kind of the harmonic wave mentioned above can accumulate with wave propagation distance and attain significant amplitude. Thus, the nonlinear process through self-interaction of one acoustic mode to generates its own harmonic is called resonant nonlinear interaction [3]. The other processes are referred to as non-resonant.

Previously the second-order nonlinearity or second harmonic generation (SHG) of transverse waves in single crystals was investigated [4] and it was observed that the second-order resonant nonlinear self-interactions of transverse waves, which corresponds to the accumulated second harmonic generation, does not exist in isotropic solids or in anisotropic crystals when the transverse wave propagates along some high symmetry directions. In the present paper the study is extended to the third-order nonlinearity or the third harmonic generation (THG) of transverse waves in isotropic solids and in anisotropic crystals when the transverse wave propagates along those directions. It is found that the accumulated third harmonic transverse wave can be generated in those high symmetry directions. Since the resonant second order nonlinearity does not exist, in other words, the first non-vanishing resonant nonlinearity of transverse waves is third-order, the third harmonic wave is generated only by cubic nonlinear self-interaction of the fundamental wave. Therefore, the THG of transverse waves is similar to the second harmonic generation (SHG) of longitudinal waves conceptually. The amplitude of the generated third harmonic wave is linearly proportional to the propagation distance. Therefore, a nonlinearity parameter characterizing the THG can be explicitly defined analogous to the SHG of longitudinal wave. The third order nonlinearity parameter involves a linear

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combination of second-, third and fourth-order elastic constants. In piezoelectric crystals, it also involves higher-order dielectric and piezoelectric constants when piezoelectric coupling exists.

The third harmonic generation (THG) of transverse waves in those high symmetry directions distinguishes from the THG of longitudinal waves. For longitudinal waves the resonant second order nonlinearity exists for all pure mode directions. The simultaneous existence of second and third order resonant self-interactions makes the third harmonic of longitudinal wave contain two contributions. The first source is the second-order interaction of the generated second harmonic with the fundamental wave. The second one is the third-order self-interaction of the fundamental longitudinal wave. In most of experimental conditions, the third harmonic wave mainly comes from the first source, as pointed out by Na and Breazeale, who observed the THG of longitudinal wave in some PZT ceramics [5]. In this case the amplitude of generated third harmonic longitudinal wave is proportional to the square of propagation distance and the nonlinearity parameter defined to characterize the THG will not involve the fourth order elastic constants.

Since the nonlinearity parameter of THG defined in this paper involves a linear combination of second-, third and fourth-order elastic constants, if the third-order nonlinearity parameter can be experimentally measured, the THG of transverse waves can be used to determine fourth-order elastic constants of materials. So far the fourth-order elastic constants could be determined only by means of pressure derivatives of third-order elastic constants [6]. High pressure is not appropriate for porous materials because the oil used as pressure transfer medium will penetrate into its pores. It is also difficult to generate high enough pressure to accurately determine the velocity curvature. The THG technique reported here does not need static pressure and is much easier to realize.

In this paper, theoretical analysis of transverse wave THG will be given. The expressions of the third order nonlinearity parameters are derived for cubic, hexagonal (622, 6mm, $\bar{6}$m2, 6/mm) and trigonal (32, 3m, $\bar{3}$m) crystals because many useful materials belong to these groups. Second, the experiment to measure the third-order nonlinearity parameter is described. Experiments are conducted for poled and unpoled PZT-4 ceramics. Pronounced third harmonic has been observed in the material. In order to measure the absolute amplitudes of the fundamental and third-harmonic waves, a calibrated contact transducer is used. From the measurements, some combinations of second-, third- and fourth-order elastic constants are determined for the PZT-4 samples.

2. The third harmonic generation of transverse wave in solids

To investigate the third order nonlinearity or THG, the state function of an electro- elastic solid needs to be expanded up to the fourth-order terms in strain and electric field. Then, the nonlinear constitutive equations up to third-order nonlinearity can be expressed as [7, 8]:

$$\begin{aligned} T_{ij} &= c_{ijkl}u_{k,l} \\ &\quad + \frac{1}{2}\left(c_{ijklmn} + \delta_{km}c_{ijnl} + 2\delta_{jm}c_{inkl}\right)u_{k,l}u_{m,n} \\ &\quad + \frac{1}{6}\left(c_{ijklmnpq} + 3\delta_{km}\delta_{pj}c_{iqnl} + 3\delta_{pj}c_{iqklmn}\right. \\ &\quad \left. + \frac{3}{2}\delta_{pm}c_{ijklqn} + \frac{3}{2}\delta_{kp}c_{ijqlmn}\right)u_{k,l}u_{p,q}u_{m,n} \\ &\quad + e_{mij}\phi_{,m} - \frac{1}{2}b_{mnij}\phi_{,m}\phi_{,n} \\ &\quad + \left(e_{mijkl} + \delta_{kj}e_{mil}\right)\phi_{,m}u_{k,l} \\ &\quad + \frac{1}{2}\left(e_{mijklpq} + \delta_{kp}e_{mijql}\right. \\ &\quad \left. + 2\delta_{pj}e_{miqkl}\right)\phi_{,m}u_{k,l}u_{p,q} \\ &\quad - \frac{1}{2}l_{mnijpq}\phi_{,m}\phi_{,n}u_{p,q} + \frac{1}{6}f_{mnpij}\phi_{,m}\phi_{,n}\phi_{,p}, \end{aligned} \tag{1a}$$

$$\begin{aligned} D_m &= -\varepsilon_{mn}\phi_{,n} + e_{mij}u_{i,j} \\ &\quad + \frac{1}{2}\left(\delta_{ik}e_{mlj} + e_{mijkl}\right)u_{i,j}u_{k,l} \\ &\quad + \frac{1}{2}\varepsilon_{mnp}\phi_{,n}\phi_{,p} - b_{mnij}\phi_{,n}u_{i,j} \\ &\quad + \frac{1}{6}\left(e_{mijklpq} + 3\delta_{kp}e_{mijql}\right)u_{i,j}u_{k,l}u_{p,q} \\ &\quad - \frac{1}{2}\left(l_{mnijpq} + \delta_{iq}b_{mnpj}\right)\phi_{,n}u_{i,j}u_{p,q}, \end{aligned} \tag{1b}$$

where T_{ij} is the total Piola-Chirhhoff stress tensor, $\boldsymbol{D}$ is material electric displacement and δ_{ij} is the Kronecker delta. In equation (1), $\boldsymbol{u}$ is particle displacement and ϕ is the electric potential function. The indices after comma in subscript stand for partial derivatives with respect to the corresponding space coordinates. The coefficients c_{ijkl}, c_{ijklmn} and $c_{ijklmnpq}$ are second-, third- and fourth-order elastic constants, e_{mij} are linear piezoelectric constants, ε_{mn}, ε_{mnp} and ε_{mnpq} are second-, third- and fourth-order dielectric permittivities, b_{mnij} are the electrostrictive tensor components, e_{mijkl} are the third-order eletroelasticity coefficients, $e_{mijklpq}$ are the odd fourth-order electroelasticity coefficients, l_{mnjipq} are the even fourth-order electroelasticity coefficients and f_{mnpij} are the fourth- order piezoelectric constants. Here, the material coordinates are always used. Except dielectric permittivity constants, all the constants can be expressed by abbreviated indices according to $11 \rightarrow 1$; $22 \rightarrow 1$; $33 \rightarrow 3$; $23, 32 \rightarrow 4$; $13, 31 \rightarrow 5$ and $12, 21 \rightarrow 6$.

The equation of motion and quasi-static electric equation can be written as:

$$\rho_0 u_j = T_{ij,i} \qquad (i, j = 1, 2, 3), \tag{2a}$$

$$D_{m,m} = 0 \qquad (m = 1, 2, 3). \tag{2b}$$

In this paper, the THG of transverse waves is investigated for certain pure mode directions. For convenience, a new coordinate system (abc), which is rotated with respect to the constitutive coordinate system (XYZ) of a crystal, is constructed according to the wave propagation

ducers are used in the experiment presented in this paper. Obviously the bonding condition will affect the sensitivity of the receiving transducer. Thus, the calibration of the receiving transducer must be done at the beginning of every round of THG experiments. Through the calibration process the bonding quality can be evaluated and we can obtain the response function used in this round of THG experiments. Because only the amplitude ratios are used, slight variation of the signal magnitude in different experiments will not affect the final results. Measurements are carried out for both poled and unpoled PZT-4 ceramics. Although the value of the nonlinearity parameter of THG is almost one order of magnitude larger than that for SHG of longitudinal waves, the nonlinear effect is usually weak because the third power of the strain associated with transverse wave is usually very small. However, the experiment presented in this paper shows that the third-harmonic wave can be detected with a good signal to noise ratio by using the experiment setup presented in this paper.

When the second- and third-order constants involved in the nonlinearity parameter are known, the fourth-order constants can be calculated from the measured third-order nonlinearity parameters. There are obvious advantages of using THG technique of transverse waves to determine the fourth-order elastic constants of materials compared to using the high pressure technique to find the curvature of pressure velocity relation, particularly for fragile and porous materials, such as ceramics. It is known that the harmonic generation technique can only determine parts of third-order elastic constants [1]. The shear third-order elastic constants that are involved in our third- order nonlinearity parameters need to be determined by using the high-pressure technique. Our results give the possibility to reliably determine some fourth order elastic constants once the third order elastic constants are determined.

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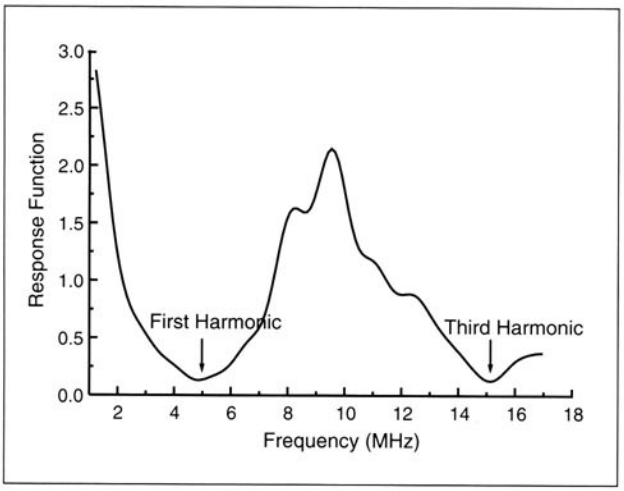

Figure 2. A typical transducer response function (Transducer: PZT-4 disc, bonding agent: Salol).

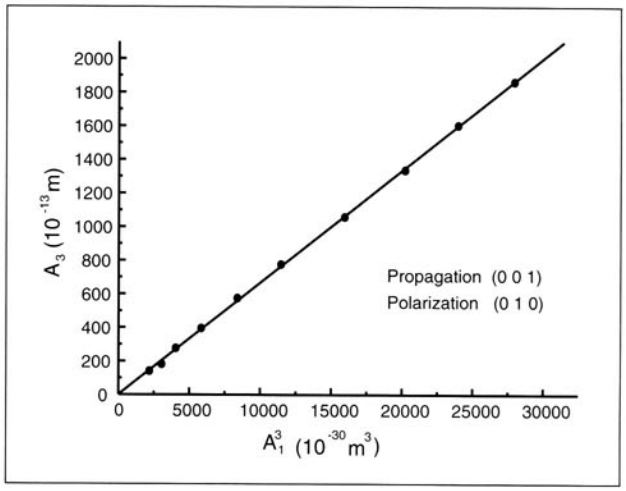

Figure 3. Variation of the third harmonic amplitude with respect to the third power of the fundamental amplitude.

The PZT-4 samples (Valpey-Fisher, Hopkington, MA) both poled and unpoled are cubes with side dimension of 2.54 cm. Figure 3 gives the variation of the third harmonic amplitude with the third power of the fundamental amplitude, measured for a poled PZT-4 sample when the wave propagates and polarizes normally to the poling direction. The straight line is expected from equation (9b). This is also a verification that the third harmonic is not generated by electronics. From the slope of the measured straight lines, the nonlinearity parameter β_3 can be obtained. The measured results for waves with various propagation and polarization directions are listed in Table II.

There may be an ambiguity for the sign of β_3 when the quadratic and cubic nonlinearities exist at the same time. When the nonlinearity is the third-order only, such as for cases discussed in this paper, the ambiguity may be eliminated. In these cases, the nonlinear strain-stress relation can be expressed as:

$$T = 2M_2\eta\left(1 - 4\beta_3\eta^2\right), \tag{14}$$

where T and η are stress and strain, respectively. For a pure mode transverse wave,

$$\eta = \frac{1}{2}\frac{\partial u}{\partial a}. \tag{15}$$

Since the strain-stress relation is usually a convex upward curve, β_3 must be positive. Consequently, the M_4 corresponding to a given β_3 can be calculated from equation (12). The results are also listed in Table II. It is observed that the sound velocity, which is determined by C_{44} for the transverse wave propagating in isotropic unpoled sample, is not much different from that for the transverse wave with both propagation and polarization directions normal to the poling direction in a poled sample. But their β_3 values are quite different. It seems that the poling process introduces some nonlinearity to the X-direction of the sample. The situation is similar to the SHG of longitudinal wave in PZT-4 [14].

Table II. The measured nonlinearity parameter of PZT-4. $\boldsymbol{N}$: wave propagation direction; $\boldsymbol{U}$: wave polarization direction. (0 0 1) is corresponding to the poling direction of PZT ceramic. Unit of M_2 and M_4 is 10^{10} N/m^2.

sample	$\boldsymbol{N}$	$\boldsymbol{U}$	β_3	M_2	M_4
poled	(0 0 1)	$\perp \boldsymbol{N}$	98.8	2.55	-249.4
	$\perp$ (0 0 1)	$\perp \boldsymbol{N}$	70.6	3.01	-212.5
	$\perp$ (0 0 1)	$\parallel$ (0 0 1)	49.7	3.92	-194.6
unpoled	arbitrary	$\perp \boldsymbol{N}$	45.8	2.86	-131

4. Conclusions

Since the second-order resonant nonlinearity of transverse waves does not exist in isotropic solids and along high symmetry directions of crystals of other symmetries, the first non-vanishing resonant nonlinearity of transverse waves is third-order. The THG of transverse waves in such systems originates solely from the cubic nonlinear self-interaction of the fundamental transverse wave. Therefore, the generated third harmonic transverse wave will accumulate with propagation distance linearly, which is similar to the second harmonic generation of longitudinal waves. Following the SHG terminology, we have defined a third-order nonlinearity parameter β_3 to characterize the THG of transverse waves. The β_3 parameter involves linear combination of second-, third- and fourth-order elastic constants, hence, can be used to measure fourth order elastic constants. As examples, expressions of the nonlinearity parameter are derived for cubic, hexagonal (622, 6mm, $\bar{6}$mm, 6/mm) and trigonal (32, 3m, $\bar{3}$m) crystals.

Experimentally, the third-order nonlinearity parameter can be determined by measuring the absolute amplitudes of the fundamental and third harmonic acoustic waves. In order to measure the absolute amplitudes of acoustic waves, capacitive detector is often used [1]. But the capacitive detector cannot response to particle displacement in plane (shear). Therefore, the calibrated contact trans-

Table I. Expressions of M_2 and M_4 for cubic, hexagonal (622, 6mm, $\bar{6}$mm, 6/mm) and trigonal (32, 3m, $\bar{3}$m) crystals. $\boldsymbol{N}$: wave propagation direction; $\boldsymbol{U}$: wave polarization direction.

Isotropic

$\boldsymbol{N}$	$\boldsymbol{U}$	M_2	M_4
Arbitrary	$\perp \boldsymbol{N}$	c_{44}	$\frac{1}{6}(3c_{11} + 6c_{166} + c_{4444})$

Cubic: θ is the angle between polarization direction and [010]. a) for class 432, m3m, $\bar{4}$3m; b) for class 23, m3; c) only for class 432,43m, m$\bar{3}$m. *: Piezoelectric coupling for class 23 and $\bar{4}$3m, $M_2 = c_{44}^D = c_{44} + e_{14}^2/\varepsilon_{11}$.

$\boldsymbol{N}$			$\boldsymbol{U}$				
N_1	N_2	N_3	U_1	U_2	U_3	M_2	M_4
1	0	0	0	$\cos\theta$	$\sin\theta$	c_{44}	a) $\frac{1}{6}\{3c_{11} + 6c_{166} + c_{4444}[1 - \frac{1}{2}\sin^2(2\theta)] + \frac{3}{2}c_{5566}\sin^2(2\theta)\}$ b) $\frac{1}{6}\{3c_{11} + 6c_{155}\sin^2\theta + 6c_{166}\cos^2\theta + c_{4444}[1 - \frac{1}{2}\sin^2(2\theta)] + \frac{3}{2}c_{5566}\sin^2(2\theta)\}$
$1/\sqrt{2}$	$1/\sqrt{2}$	0	0	0	1	c_{44}^*	a) $\frac{1}{12}(6c_{11} + 6c_{144} + 6c_{166} + 12c_{456} + c_{4444} + 3c_{4455})^*$ b) $\frac{1}{12}[6c_{11} + 6c_{144} + 3(c_{155} + c_{166}) + 12c_{456} + c_{4444} + 3c_{4455}]^*$
$1/\sqrt{2}$	$1/\sqrt{2}$	0	$-1/\sqrt{2}$	$1/\sqrt{2}$	0	$\frac{1}{2}(c_{11} - c_{12})$	c) $\frac{1}{48}(12c_{11} + 12c_{12} + 24c_{44} + 9c_{111} - 12c_{112} + c_{1111} - 4c_{1112} + 3c_{1122})$

Hexagonal: (622, 6mm, $\bar{6}$m2, 6/mm) θ is the angle between polarization direction and [100]. *: Piezoelectric coupling direction $M_2 = c_{44}^D = c_{44}^E + e_{15}^2/\varepsilon_{11}$; $M_4 = \frac{1}{6}[3c_{11}^E + 6c_{155}^E + c_{4444}^E + 4(e_{15}^2/\varepsilon_{11})(3e_{115} + e_{1555}) - 6(e_{15}^2/\varepsilon_{11})^2 l_{155} + 4(e_{15}^2/\varepsilon_{11})^3 f_{1115} - (e_{15}^2/\varepsilon_{11})^4 \varepsilon_{1111}]$.

$\boldsymbol{N}$			$\boldsymbol{U}$				
N_1	N_2	N_3	U_1	U_2	U_3	M_2	M_4
0	0	1	$\cos\theta$	$\sin\theta$	0	c_{44}	$\frac{1}{6}(3c_{33} + 6c_{344} + c_{4444})$
1	0	0	0	1	0	$\frac{1}{6}(c_{11} - c_{12})$	$\frac{1}{6}(3c_{11} + 6c_{166} + c_{6666})$
0	1	0	1	0	0		$\frac{1}{6}(3c_{11} + 6c_{266} + c_{6666})$
1	0	0	0	0	1	c_{44}^*	$\frac{1}{6}(3c_{11} + 6c_{155} + c_{4444})^*$
0	1	0					

Trigonal: (32, 3m, $\bar{3}$m)

$\boldsymbol{N}$			$\boldsymbol{U}$				
N_1	N_2	N_3	U_1	U_2	U_3	M_2	M_4
0	1	0	1	0	0	c_{66}	$\frac{1}{6}(3c_{11} + 6c_{266} + c_{6666})$

receiving transducer is shown in Figure 2. One can see that the sensitivity of the transducer at the third harmonic frequency (15 MHz) is almost the same as that at the fundamental frequency (5 MHz). The transducer is a PZT-4 disc and the bonding agent between the transducer and sample is Salol. The sample is also a poled PZT-4 ceramic, so the acoustic impedance matching is very good between the transducer and the sample. We have conducted calibration for every round of experiment in the frequency range that covers the fundamental and third harmonic frequencies, which takes care of the effect of bonding. The RF tone-burst signal applied to the transmitting transducer is filtered by a lowpass filter to avoid feeding in possible electrical third harmonic. Also, the Hanning weighted tone-burst signal is used to avoid the third harmonic to be excited by the steep edges of input RF toneburst signal.

The nonlinearity parameter β_3 can be experimentally determined by measuring A_1 and A_3:

$$\beta_3 = \frac{8}{k^3 L}\left(\frac{A_3}{A_1^3}\right). \tag{11}$$

Hence, M_4, which contains a linear combination of second-, third- and fourth-order elastic constants can be obtained:

$$M_4 = -\beta_3 M_2. \tag{12}$$

Based on the constitutive equation (1), the expressions of M_2 and M_4 for isotropic solids, cubic, hexagonal (622, 6mm, $\bar{6}$m2, 6/mm) and trigonal (32, 3m, $\bar{3}$m) crystals are calculated and the results are listed in Table I. The wave propagation and polarization directions are also indicated in the Table. For the transverse waves with those selected propagation and polarization directions, the second-order resonant nonlinearity does not exit. The independent fourth-order elastic constants for above materials can be found from the work of Chung [10]. The contribution of piezoelectric coupling to M_2 and M_4 has been estimated for the transverse wave propagating along [100] and polarizing along [001] in crystal of 6mm symmetry and the result is also listed in Table I.

3. Experiment

We have conducted THG experiments of transverse waves in poled and unpoled PZT-4 ceramic. Poled PZT ceramics have conic symmetry of ∞m. Their material constant tensors of order lower than sixth are the same as those for the crystals with 6mm symmetry [11]. The third- and fourth-order elastic constants are sixth- and eighth-order tensors, respectively. They are generally different from 6mm for an ∞m system. It has been pointed out that there is an additional relationship of $c_{166} = c_{266}$ for ∞m system. Hence, the number of independent third-order elastic constants is 9 for ∞m, but 10 for 6mm system [12]. Thus, whether or not the results calculated for 6mm system can be used for PZT materials needs to be examined carefully. It is known that the poling direction, i.e. Z-axis, of PZT ceramics corresponds to the ∞-fold symmetry axis. In the plane perpendicular to this axis the material properties exhibit isotropic. Thus, expressions of M_4 for ∞m system must conform with the transverse symmetry. It can be seen from Table I that M_4 of the transverse wave propagating along the Z-axis of a 6mm crystal is polarization independent, therefore, transversely isotropic. The expression of M_4 for the transverse wave propagating along poling direction in PZT ceramics must be the same. For the transverse wave with the polarization parallel to the Z-axis, the M_4 is different when the wave propagates along X-axis and along Y-axis in a 6mm system. But there is a relation $c_{166} = c_{266}$ for an ∞m system as mentioned above [12], which makes M_4 isotropic. Therefore, all the expressions of M_4 listed in Table I for 6mm system can be used for

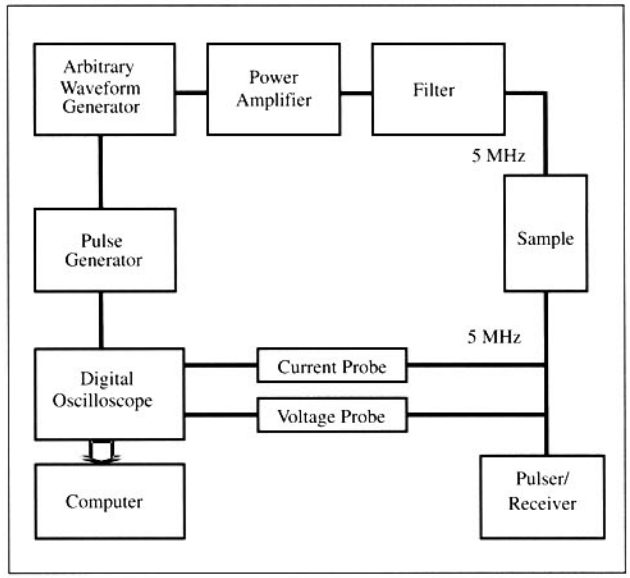

Figure 1. The experimental setup.

materials with ∞m symmetry. In su mmary, the following M_4 can be determined through THG measurements in poled PZT ceramics.

1. $M_4 = (1/6)(3c_{33} + 6c_{344} + c_{4444})$ for the transverse wave propagating along poling direction;
2. $M_4 = (1/6)(3c_{11} + 6c_{166} + c_{6666})$ for the transverse wave with both the propagation and polarization normal to the poling direction;
3. $M_4 = (1/6)(3c_{11} + 6c_{155} + c_{4444})$ for the transverse wave with propagation normal to and polarization parallel to the poling direction.

In case 3, the piezoelectric effect exists, therefore, the M_4 is an effective one including the piezoelectric contribution. Unpoled PZT can be treated as isotropic, from THG experiment $M_4 = (1/6)(3c_{11} + 6c_{166} + c_{4444})$ can be determined.

The experiment setup is shown in Figure 1, which is the same as that used for the second harmonic generation except that the receiving transducer with the same center frequency as the transmitting transducer is used because a transducer can operate at fundamental and all its odd harmonic frequencies. In other words, the receiving transducer centered at the fundamental frequency can respond to both the fundamental and the third harmonic waves.

In order to measure the absolute amplitude of the acoustic waves, the receiving transducer is calibrated by following the procedure given by Dace [13]. Through the calibration, a so-called response function of the transducer $H(\omega)$ can be obtained. The amplitude of the acoustic wave $A(\omega)$ at frequency ω is obtained through the formula:

$$A(\omega) = \left|I(\omega)\right| \cdot \left|H(\omega)\right|, \tag{13}$$

where $I(\omega)$ is the output current of the receiving transducer at frequency ω. One typical response function of the

and polarization direction. In the (abc) system, axis a is always chosen to coincide with the wave propagation direction while b and c to be along possible polarization directions of the wave. Through a coordinate transformation, a plane wave originally propagating along a pure mode direction in system (XYZ) becomes a plane wave propagating along a-axis in the (abc) system. The particle displacement and electric potential are only functions of coordinate a, therefore, equation (2) may be simplified to one-dimensional. For a pure mode wave, it can be assumed that only one of the particle displacement components and hence the associated electric field is non-zero. Substituting the constitutive equation (1) into equations (2), a set of acoustic-electric coupling equation can be obtained. From (2b) the piezoelectrically generated electric potential ϕ can be expressed by the particle displacements. Then, (2a) becomes a third-order nonlinear wave equation which can be written as:

$$\rho_0 \frac{\partial^2 u}{\partial t^2} - M_2 \frac{\partial^2 u}{\partial a^2} = \frac{\partial}{\partial a}\left[M_3 \left(\frac{\partial u}{\partial a}\right)^2 + M_4 \left(\frac{\partial u}{\partial a}\right)^3\right], \quad (3)$$

which is similar to that given in reference [9]. Since there is only one displacement component in the problem, the subscript of u is ignored. Here the non-resonant nonlinear terms are omitted because the harmonic waves generated by those terms cannot accumulate with propagation and they are very weak as mentioned above. In equation (3) M_2 contains the relevant second-order elastic constants or their combination, which is associated with sound velocity of small amplitude acoustic wave; M_3 and M_4 are the coefficients of second-order and third-order nonlinear terms, respectively. The former involves the second- and third-order elastic constants or their combination. The later involves the second-, third- and fourth-order elastic constants or their combination. In the case of the piezoelectric coupling, they represent stiffened or effective constants [4].

Equation (3) may be solved by successive approximation method. Let

$$u = \lambda u^{(1)} + \lambda^2 u^{(2)} + \lambda^3 u^{(3)} + \ldots, \quad (4)$$

where λ is a factor indicating the order of magnitude of the successive terms. By equating the terms with the same order of magnitude, the following equations are obtained:

$$\rho_0 \frac{\partial^2 u^{(1)}}{\partial t^2} - M_2 \frac{\partial^2 u^{(1)}}{\partial a^2} = 0, \quad (5a)$$

$$\rho_0 \frac{\partial^2 u^{(2)}}{\partial t^2} - M_2 \frac{\partial^2 u^{(2)}}{\partial a^2} = M_3 \frac{\partial}{\partial a}\left[\left(\frac{\partial u^{(1)}}{\partial a}\right)^2\right], \quad (5b)$$

$$\rho_0 \frac{\partial^2 u^{(3)}}{\partial t^2} - M_2 \frac{\partial^2 u^{(3)}}{\partial a^2} = M_3 \frac{\partial}{\partial a}\left(\frac{\partial u^{(1)}}{\partial a}\frac{\partial u^{(2)}}{\partial a}\right) + M_4 \frac{\partial}{\partial a}\left(\frac{\partial u^{(1)}}{\partial a}\right)^3. \quad (5c)$$

Equation (5a) is a usual linear wave equation, its solution can be written as

$$u^{(1)} = A_1 \sin\left(\omega t - ka\right), \quad (6a)$$

where k is the wave number and A_1 is the amplitude of the fundamental wave. Substituting (6a) into (5b) yields

$$u^{(2)} = -\frac{1}{4} k^2 A_1^2 a \left(\frac{M_3}{M_2}\right) \cos\left[2(\omega t - ka)\right], \quad (6b)$$

(where only the second harmonic particular solution is given, the zero frequency component is omitted). From equation (5c), it is seen that the third harmonic can be generated by the second-order nonlinear interaction of the generated second harmonic $u^{(2)}$ and the fundamental wave $u^{(1)}$, as well as by the third-order nonlinear interaction of the fundamental wave $u^{(1)}$. They correspond to the first and the second terms in the right-hand side of equation (5c), respectively. In this case, the third harmonic particular solution is expressed as:

$$u^{(3)} = B \sin\left[3(\omega t - ka)\right] + C \cos\left[3(\omega t - ka)\right]. \quad (7)$$

In equation (7),

$$B = -\frac{1}{8}\left(\frac{M_3}{M_2}\right)^2 k^4 A_1^3 L^2, \quad (8a)$$

$$C = -\frac{1}{6}\left[\left(\frac{M_3}{M_2}\right)^2 - \frac{3}{4}\left(\frac{M_4}{M_2}\right)\right] k^3 A_1^3 L, \quad (8b)$$

where L is the distance along the wave propagation direction (or the length of the sample). For longitudinal waves, the second-order and third-order resonant nonlinearities exist simultaneously i.e., $M_3 \neq 0$ and $M_4 \neq 0$. But in most experimental conditions, the third harmonic generation of longitudinal waves is mainly from the second-order nonlinear interaction as pointed out in reference [5]. C can be ignored compared to B, therefore, the nonlinearity parameter of THG will not involve the fourth-order constants. However, for transverse waves, the second-order resonant nonlinearity does not exist for isotropic solids and in some high symmetry directions of anisotropic materials [2, 4]. In this case $M_3 = 0$, hence $B = 0$ and the third-harmonic solution (7) can be simplified as

$$u^{(3)} = A_3 \cos\left[3(\omega t - ka)\right], \quad (9a)$$

where

$$A_3 = \frac{1}{8}\left(\frac{M_4}{M_2}\right) k^3 A_1^3 L. \quad (9b)$$

Analogous to the case of second harmonic generation, a third-order nonlinearity parameter characterizing the THG may be defined:

$$\beta_3 = -\frac{M_4}{M_2}. \quad (10)$$