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# Ultrasonic nonlinearity of regular and relaxor ferroelectric ceramics*

JIANG Wenhua (姜文华)[1] and CAO Wenwu (曹文武)[2]

1. Institute of Acoustics and State Key Laboratory of Modern Acoustics, Nanjing University, China
2. Materials Research Laboratory, Pennsylvania State University, USA

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**Abstract** Ultrasonic nonlinear properties of ferroelectric lead zirconate-titanate (PZT) and relaxor PMN-PT ceramics are investigated by using ultrasonic second harmonic generation technique. The ultrasonic nonlinearity of regular piezoelectric ceramics is found to be in the range expected for most solid materials whereas relaxor material PMN-PT exhibits very strong ultrasonic nonlinearity.

**Keywords:** ultrasonic nonlinearity, ferroelectric ceramics.

As leading piezoelectric materials piezo-ceramics are widely used in ultrasonic transducer, resonator, sensor, ultrasonic motor, actuator etc. The investigation of their nonlinear properties is important since some of piezoelectric devices are driven far out of the linear regime. Beige has measured the nonlinear elastic coefficient $s_{333}{}^{E}$ and the nonlinear dielectric coefficient $\varepsilon_{3333}{}^{T}$ as well as their temperature dependence for some modified lead zirconate-titanate ceramics (Piezolan $S_2$, L $T_m$ ) by means of the resonance method[1]. Na and Breazeale had measured the third-order elastic constants $C_{111}{}^{E}$ and $C_{333}{}^{D}$ of PZT ceramics K1 and S1 by means of ultrasonic second harmonic generation (SHG) technique[2]. In the present paper the nonlinear properties of the popularly used PZT ceramics, such as PZT-4, PZT-5A and PZT-5H etc. and relaxor PMN-PT are studied also by the SHG technique. The distinctions are found to exist in the nonlinear coefficients of the different group of sample.

## 1 Experimental determination of nonlinearity parameter

The SHG of the longitudinal wave in piezoelectric crystals has been investigated[2,3]. It is found the piezoelectric coupling usually enhances the nonlinearity, which results in an effective nonlinearity parameter. Thus the bilinear equation for an electro-elastic crystal can be written in several as:

$$\rho_0 \ddot{u} - K_2 u_{aa} = (3K_2 + K_3) u_a u_{aa} \tag{1}$$

where $u$ is particle displacement. $K_2$ is constant-field or stiffened second-order elastic constants or their combination, $K_3$ is constant-field or effective third-order elastic constant or their combination, depending on whether the wave propagation direction is piezoelectric coupling or not. It is known that the solution of Eq. (1) is

$$u = A_1 \sin\psi + A_2 \cos(2\psi) , \quad \psi = \omega t - ka \tag{2}$$

where $A_2$ is the amplitude of the second harmonic wave

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$$A_2 = -\tfrac{1}{8}k^2 L\beta A_1^2 \tag{3}$$

and $\beta$ is the ultrasonic nonlinearity parameter:

$$\beta = -\frac{3K_2 + K_3}{K_2} \tag{4}$$

which may be constant-field or effective quantity depending on whether the piezoelectric coupling exists or not. Thus $\beta$ can be experimentally determined by measuring absolute amplitudes of the fundamental and the second harmonic waves.

$$\beta = \frac{8}{k^2 L}\left(\frac{A_2}{A_1^2}\right) \tag{5}$$

where $k$ is the wavenumber and $L$ is the sample length.

The experimental setup is shown in figure 1. To get the absolute amplitude of the acoustic waves the receiving transducer centered at the second harmonic frequency is calibrated by the procedure given in[4]. The 10 MHz or 5 MHz are chosen as the fundamental frequency. Thus the second harmonic are 10 or 20 MHz.

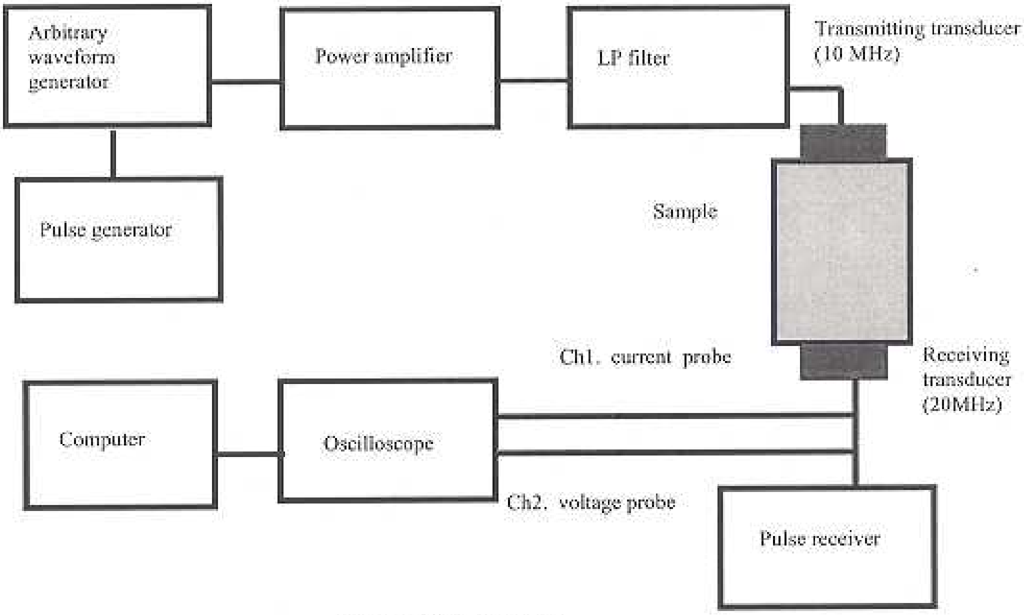

Fig.1 Experimental setup.

## 2 Results and discussions

The ultrasonic nonlinearity parameter $\beta$ was measured for PZT-4, PZT-5A, PZT-5H as well as relaxor PMN-PT. The PZT samples are from Valpey-Fisher (Hopkinton, MA) and the Lanthanum doped PMN-PT sample is from TRS Ceramics (State College, PA). The measured results are listed in the table I. From $\beta$ the third-order elastic constants $C_{111}{}^{E}$ and $C_{333}{}^{D}$ are obtained for the poled samples. The third-order elastic coefficient $C_{111}$ is obtained for the unpoled and depoled samples.

For poled PZT-4 and PZT-5A, the $\beta$ value in the Z-direction is comparable with that of single crystals[5]. The same conclusion was also given in Ref. 2. If we identify the porosity of the PZT materials measured in our experiment according to their density, sound velocity and acoustic attenuation, the poled high density PZT-5H (PZT-5H HD) has the highest density, highest velocity and lowest attenuation among the measured materials. It is seen from Table I that PZT-5H HD has the smallest nonlinearity parameter $\beta$ compared with other Z-cut PZT materials. The regular PZT-5H has the lowest density, lowest sound velocity and largest attenuation among the measured materials. Its $\beta$ is five times as large as the $\beta$ value of PZT-5H HD. The porosity of PZT-5A is in between PZT-5H HD and PZT-5H. Its $\beta$ value in Z-direction is also in between PZT-5H HD and PZT-5H. Comparing the $\beta$ value of PZT-5H HD, PZT-5A and PZT-5H, it can be concluded that more porous material has larger nonlinearity. It was pointed out by Donskoy et al that the $\beta$ value of some porous materials, such as rocks, could be as large as $10^3$-$10^4$ [6]. Thus it seems to be reasonable to believe that the porosity has some contributions to nonlinearity of regular PZT-5H. On the other hand, the $\beta$ values of the single crystals are reported in the range of 2-14[5]. For regular PZT-5H, although its β is a little out of the normal range, it is still in the context of nonlinear acoustics of crystals.

Table 1 Sample parameter and the measured results for PZT-4, PZT-5A, PZT-5H (HD) PZT-5H and PMN-PT

| sample | PZT-4 | | | PZT-5A | | | PZT-5H HD | | PZT-5H | | PMN-PT |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | poled | | unpoled | poled | | unpoled | poled | depoled | poled | depoled | unpoled |
| Orientation | Z-cut | *X*-cut | isotropic | Z-cut | *X*-cut | isotropic | Z-cut | isotropic | Z-cut | isotropic | isotropic |
| Shape | cubic$^{1)}$ | cubic$^{1)}$ | cubic$^{1)}$ | cubic$^{1)}$ | cubic$^{1)}$ | cubic$^{1)}$ | plate$^{2)}$ | plate$^{2)}$ | plate$^{3)}$ | plate$^{2)}$ | cylinder |
| $r$ (kg/m$^3$) | 7600 | 7600 | 7600 | 7500 | 7500 | 7500 | 7800 | 7800 | 7500 | 7500 | 7800 |
| Porosity | 0.95 | 0.95 | 0.95 | 0.94 | 0.94 | 0.94 | 0.98 | 0.98 | 0.94 | 0.94 | 0.96 |
| $K_2^{4)}$ | 14.7 | 13.2 | 13.2 | 14.1 | 11.7 | 11.7 | 17.1 | 13.5 | 13.4 | 10.6 | 14.1 |
| b | 7.03 | 19.5 | 16 | 5.1 | 4.5 | 2.9 | 3.2 | 8.3 | 15 | 18.3 | 30 |
| $K_3^{5)}$ | -14.7 | -29.7 | -25.1 | -11.4 | -8.8 | -6.9 | -10.6 | -15.3 | -24.1 | -22.6 | -465.3 |

1) 25.4 mm cube; 2) 25.4 × 25.4 × 6.3 mm$^3$; 3) Disk of 25.4 mm diameter and thickness 12.7 mm;
4) Unit: $10^{10}$ N/m; 5) Unit: $10^{11}$ N/m$^2$.

PZT-4 ceramic is an exception to the above empirical rule; it is more porous than PZT-5H HD but less porous than PZT-5A according to its density. Although the rules for the sound velocity and acoustic attenuation are obeyed, its $\beta$ value in the Z-direction is larger than that of PZT-5A. The *X*-direction and the unpoled sample also exhibit stronger nonlinearity. This means that, in addition porosity of the materials, there are some other factors influencing the nonlinearity of PZT materials.

In the experiment, it is found that the sound velocities are the same for an unpoled PZT sample and the *X*-direction of a corresponding poled PZT sample for both PZT-4 and PZT-5A. But the nonlinearity parameter $\beta$ of an unpoled sample is a little different from the $\beta$ of the *X*-direction of a corresponding poled sample. Because the *X*-direction is not influenced by the polarization, the poling process seems to generate some porosity in the sample, in other words, a slight volume increase may have occurred, which has been ignored since most of the density measurements are not sensitive enough to detect it.

To see the poling influence, the poled PZT-5H HD and poled regular PZT-5H samples were thermally depoled. Then the nonlinearity parameters of depoled samples were measured. The results are also listed in the table 1. It is observed that the depoling process reduces the sound velocity of PZT-5H HD by about 10%. But the nonlinearity parameter increases by three times. The result shows the fact again that the nonlinear parameters are more sensitive to structural variation of the material than the linear parameters do. The situation is a little different for the regular PZT-5H. The depoling process makes its sound velocity decrease by 10%, its nonlinearity parameter has no much change. This may be understood by the fact that regular PZT-5H is more porous and the depoling process has no much contribution to its variation of structure.

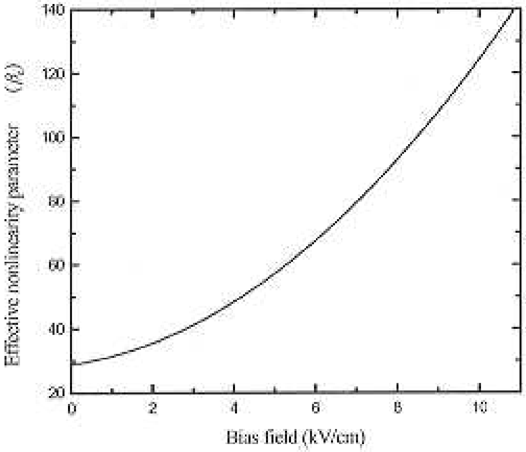

Fig. 2 The $\beta$ value under the different bias electric field for (MN-PT).

Relaxor PMN-PT is a very strong electrostrictive material. This intrigued many researchers to study its elastic, dielectric and electrostrictive properties[7]. In those studies, however, linear elasticity of the material was assumed although very strong nonlinear relations were observed between field-induced properties and applied electric field[7]. In some cases the assumption of linear elasticity may not be valid since very strong elastic nonlinearity was observed for the measured PMN-PT. Its $\beta$ value is 30, which is much larger than regular PZT ceramics. Usually the electrostrictive material is used under electric bias field. Under this case, it is found that its nonlinearity parameter is adjustable by applied bias field. Fig. 2 gives the calculated effective $\beta$ under the different bias electric field. The nonlinear parameter will increase by three times when applied bias field increasing from zero to 10 kV/cm. This feature may be benefit to some nonlinear piezoelectric devices.

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