

# High-frequency dispersion of ultrasonic velocity and attenuation of single-crystal $0.72 \text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.28 \text{PbTiO}_3$ with engineered domain structures

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Using ultrasonic spectroscopy, the frequency dispersions of ultrasonic velocity and attenuation were measured for single crystal  $0.72 \text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}) - 0.28 \text{PbTiO}_3$  (PMN-28%PT) with engineered domain structures in the frequency range of 50–110 MHz. We found that the velocity dispersion and attenuation are very small for the longitudinal wave propagating along [001] of the pseudotetragonal state. Our results imply that the developed domain-engineered PMN-PT single crystals, which have extremely large  $d_{33}$  and  $k_{33}$ , have great potential for high-frequency applications. © 2002 American Institute of Physics. [DOI: 10.1063/1.1468265]

Piezoelectric (PZT) ceramics have been the dominant ultrasonic transducer materials since their discovery more than 40 years ago. But they exhibit high attenuation and large velocity dispersion at high frequencies due to the strong scattering of acoustic waves at the grain boundaries.<sup>1</sup> Therefore, for frequencies above 25 MHz, single-crystals  $\text{LiNbO}_3$  or quartz are exclusively used for making ultrasonic transducers. Although those single crystals have negligible attenuation and dispersion at frequencies up to several hundreds megahertz, their electromechanical coupling coefficients and piezoelectric coefficients are much too low.

Recently, relaxor-based single crystals  $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3}) - x\text{PbTiO}_3$  (PZN-PT) and  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}) - x\text{PbTiO}_3$  (PMN-PT) have emerged to be much superior piezoelectric materials. They have very large  $d_{33}$ , ranging from 2000–2500 pC/N and the electromechanical coupling coefficient  $k_{33}$  is greater than 90%.<sup>2–5</sup> Such a high coupling coefficient and large piezoelectric coefficient are very attractive for making broadband ultrasonic transducers. The large  $d_{33}$  and  $k_{33}$  of those single crystals originate from engineered domain structures, which are the result of poling the single crystals with rhombohedral symmetry along [001] of cubic axis to make them into desired multidomain structures. For the multidomain single crystals, an important question arises: “Are their attenuation and velocity dispersion as low as other single-domain single crystals, such as  $\text{LiNbO}_3$  or quartz?” After all, the ultrasonic attenuation is closely associated with the presence of domains. Using the ultrasonic spectroscopy technique, we have investigated a PMN-28%PT single crystal in the frequency range of 50–110 MHz. The results are surprisingly encouraging, the attenuation and velocity dispersion both are very small, making these crystals good candidates for high frequency medical ultrasonic transducers.

The PMN-PT crystal specimen was made from a single-crystal boule of type A of a PMN-PT crystal for actuator

application (H. C. Materials Co.). The PMN-PT single-crystal boule was grown by a vertical Bridgman-Stockbarger method using a sealed platinum crucible with (001) seeding. The starting raw chemicals,  $\text{PbO}$ ,  $\text{MgO}$ ,  $\text{Nb}_2\text{O}_5$ , and  $\text{TiO}_2$ , had a high purity of better than 99.99%. The starting powders were weighed to be the chemical ratio as the formula  $(1-x)\text{PMN} - x\text{PT}$  ( $x=0.28$ ) and were mixed thoroughly in an agate mortar and pestle, and then loaded into the platinum crucible. The maximum temperature in the furnace was 1395 °C and the crystal grew at the rate of 0.8 mm/hr under the temperature gradient of 20 °C/cm.

After crystallographic orientation testing was performed on a DX-4 x-ray single-crystal orientation unit, the crystal was cut into the dimensions of 18 mm × 13 mm × 2.35 mm with orientations [100]/[010]/[001] in reference to the cubic coordinates. The basal rectangular planes of 18 × 13 mm<sup>2</sup> were {001} faces. The surfaces were finished by polishing with 3 μ alumina powder. Crystal poling was performed using a 5 kV/cm electrical field applied along [001], i.e., the 2.35 mm dimension, at 23 °C after sputtering Pd/Au of 0.05 μm/0.45 μm thickness on both basal planes. Initially, tested data of the specimen gave  $d_{33} \sim 1400$  pC/N (on a Berlincourt type meter), free dielectric constant of 4300 and  $\tan \delta < 0.2\%$  (1 kHz and at 23 °C).

The ultrasonic spectra of PMN-PT single crystals were measured by using a through-transmission technique. The experiment setup was similar to that described in Ref. 1. A pair of immersion-type transducers centered at 100 MHz (E9934, Valpey-Fisher, Hopkinton, MA) was used. The transducers were immersed in a water tank and carefully aligned. The transmitting transducer driven by a pulser/receiver (5900 PR, Panametrics, Waltham, MA) launched a broadband ultrasonic pulse. Transmitted signals, for the cases of without and with the sample in between the transducers, were detected by the receiving transducer and recorded in a digital oscilloscope (TDS 430 A Tektronix), then downloaded to a computer where the fast Fourier transform (FFT) of the time domain signals was performed. The frequency-

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dependent attenuation  $\alpha(\omega)$  and the inverse velocity or the slowness dispersion  $u(\omega)$  can be obtained from<sup>1</sup>

$$\alpha(\omega) = \alpha_w(\omega) + \ln\left(T \frac{A_w(\omega)}{A_s(\omega)}\right), \quad (1)$$

$$u(\omega) = \frac{1}{V_s(\omega_0)} - \frac{1}{V_s(\omega)} = \frac{[\varphi_w(\omega_0) - \varphi_s(\omega_0)]}{\omega_0 d} - \frac{[\varphi_w(\omega) - \varphi_s(\omega)]}{\omega d}, \quad (2)$$

where  $A$  and  $\varphi$  represent amplitude and phase spectra of the detected signals, respectively. The subscript  $W$  and  $S$  stand for the spectra of the signals without and with the sample in between the transducers, respectively,  $\omega_0$  is a reference frequency chosen inside the bandwidth of the transducers,  $V_s$  is the velocity in the sample, and  $d$  is the sample thickness.  $T$  is the transmission coefficient for the acoustic wave from water to sample or from sample to water, which is independent of frequency for thick enough samples.

Although the crystal symmetry is  $3m$ , the poled multidomain crystal has a macroscopic symmetry of  $4mm$ . The longitudinal wave propagating along  $[001]$  direction of a  $4mm$  crystal is a pure-mode wave. Therefore, the transmission coefficient  $T$  can be simply calculated by

$$T = \frac{4\rho_s\rho_wV_sV_w}{(\rho_sV_s + \rho_wV_w)^2}, \quad (3)$$

for the normal incident acoustic wave.<sup>1</sup> In Eq. (3),  $\rho_s$  and  $\rho_w$  are mass density of the sample and water, respectively, and  $V_w$  is the wave velocity in water. For the measured sample  $\rho_s = 8.13$  (g/cm<sup>3</sup>). In order to obtain the dispersion of the absolute velocity, the sound velocity in the sample was measured using a conventional pulse-echo method at the reference frequency  $\omega_0$ , selected in the experiment, in our case 50 MHz. The absolute velocity dispersion is then derived from

$$V(\omega) = \frac{V(\omega_0)}{1 - u(\omega)V(\omega_0)}. \quad (4)$$

Previously, the velocity dispersion was calculated by<sup>1</sup>

$$V(\omega) = \frac{V_w}{1 + \frac{[\varphi_s - \varphi_w + \omega(t_s - t_w)]V(\omega_0)}{\omega d}}, \quad (5)$$

where  $t_s$  and  $t_w$  are the delay time for bringing the detected signals into the time window of the oscilloscope for the case with and without the sample in between the transducers, respectively. The advantage of calculating the slowness dispersion by using Eq. (3) instead of calculating the velocity dispersion using Eq. (4) is that the calculation of the velocity dispersion does not depend on the sound velocity of water, which is temperature sensitive. It is also independent of the measurement of delay time, as pointed out in Ref. 6.

The measured results of frequency-dependent attenuation and slowness dispersion of PMN-28%PT single crystal are shown in Figs. 1 and 2. For comparison, the attenuation and dispersion of PZT-4 ceramic sample (Valpey-Fisher, Hopkinton, MA) were also measured and are also shown in Figs. 1 and 2. It was observed that the attenuation and dis-

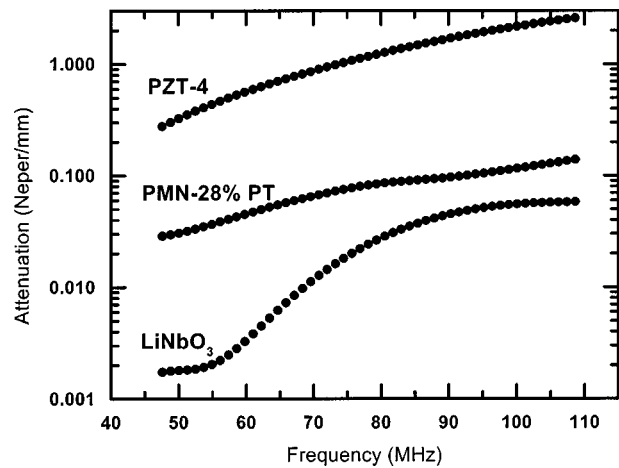


FIG. 1. Ultrasonic attenuation for PMN-28%PT multidomain single-crystal, PZT-4 ceramic and LiNbO<sub>3</sub> single domain single crystal.

persion of PMN-PT single crystal is much smaller than that of PZT-4 ceramic, which has the lowest attenuation in the family of PZT ceramics. The frequency dispersion of velocity and attenuation were also measured for a  $z$ -cut single-crystal LiNbO<sub>3</sub> sample (Valpey-Fisher, Hopkinton, MA). The results are also shown in Figs. 1 and 2. It is seen that the frequency dispersion of the phase velocity of PMN-28%PT single crystal is comparable to that of LiNbO<sub>3</sub>, whereas its attenuation is larger than that of LiNbO<sub>3</sub>. This indicates that the multidomain structures of the single crystal do have some contributions to its attenuation. In spite of this, the attenuation value is still very small compared to that of PZT-4 and is acceptable for many applications.

It is known that the longitudinal wave propagating along  $[001]$  of a  $4mm$  crystal is a piezoelectrically stiffened acoustic wave. Its velocity is correlated to the piezoelectrically stiffened elastic stiffness constant  $c_{33}^D = c_{33}^E + e_{33}^2/\epsilon_{33}^S$

$$V = \sqrt{\frac{c_{33}^D}{\rho}}. \quad (6)$$

Here, the superscript  $E$  stands for constant electric field condition,  $e_{33}$  is the piezoelectric stress constant, and  $\epsilon_{33}^S$  is the clamped dielectric permittivity. When the attenuation is

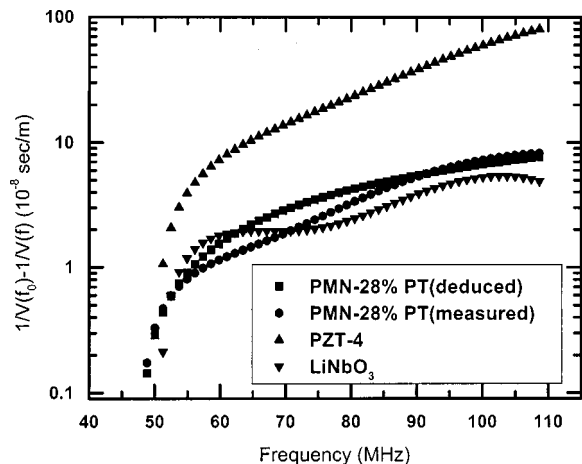


FIG. 2. Ultrasonic slowness dispersion for PMN-28%PT multidomain single crystal, PZT-4 ceramic and LiNbO<sub>3</sub> single crystal.

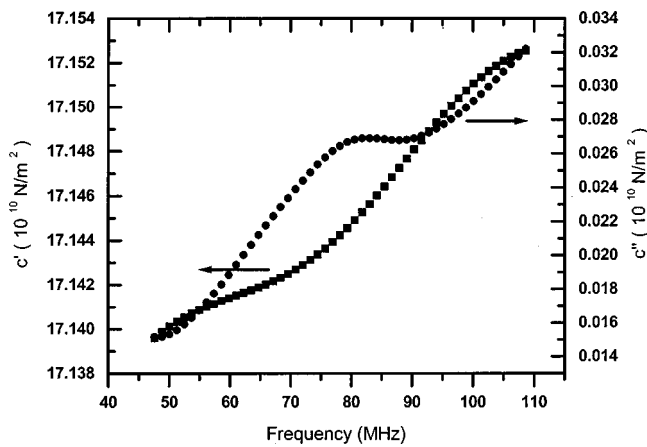


FIG. 3. Frequency dependence of real and imaginary parts of elastic constant  $c_{33}^D$  of PMN-28%PT multidomain single crystal.

taken into account, the wave number  $k = \omega/V$  can be considered a complex number, hence, the elastic constant is also a complex number, i.e.,

$$c_{33}^D = c' + jc'' \quad (7)$$

Usually  $c'' \ll c'$ . The real part and imaginary parts of the elastic constant are related to the measured phase velocity and attenuation by

$$c' \approx \rho V^2 \quad (8)$$

and

$$c'' \approx \frac{\rho V^3 \alpha}{\pi f}, \quad (9)$$

where  $f$  is the frequency. From the measured frequency-dependent attenuation and phase velocity of PMN-28% PT single crystal, the real and the imaginary parts of the elastic constant  $c_{33}^D$  were calculated and the results are shown in Fig. 3.

It is known that the velocity dispersion for an acoustic wave propagating in an unbounded medium is caused only by the attenuation.<sup>6</sup> In this case, the real and imaginary parts of the wave number, or phase velocity and attenuation, are correlated to each other through the ultrasonic Kramers–Kronig relationship.<sup>1,7</sup> Therefore, the phase velocity dispersion can be derived from the measured frequency-dependent attenuation. The velocity dispersion derived from the measured attenuation of PMN-PT single crystal is also shown in Fig. 2. Here the nearly local model of ultrasonic Kramers–Kronig relationship has been used.<sup>7</sup> It is seen that the agreement between measured and deduced velocity dispersion is fairly good.

In summary, the frequency-dependent ultrasonic attenuation and phase velocity dispersion for the longitudinal wave propagating along [001] in PMN-28%PT single crystal with engineered domain structures are measured in the frequency range of 50–110 MHz by an ultrasonic spectroscopy technique. The multidomain single crystal exhibits very low attenuation and small velocity dispersion at the measured frequency range. Considering its extremely large  $d_{33}$  and  $k_{33}$ , the single crystal has a great potential for making high frequency ultrasonic transducers.

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