# Frequency dispersion of ultrasonic velocity and attenuation of longitudinal waves propagating in $0.68Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3$ single crystals poled along [001] and [110]

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(Received 13 January 2005; accepted 7 September 2005; published online 24 October 2005)

Using ultrasonic spectroscopy, the frequency dispersion of ultrasonic velocity and attenuation in the frequency range of 50–110 MHz were measured for longitudinal waves propagating in $0.68Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3$ (PMN-32%PT) single crystals poled along [001] and [110], respectively. The measured dispersion of longitudinal wave velocity and attenuation in the multidomain PMN-32%PT crystals are smaller than that of PZT-4 but much higher than that of PMN-28%PT poled along [001]. The correlation between larger piezoelectric coefficient and higher attenuation of ultrasonic waves in multiple-domain $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ single crystal for compositions closer to the morphotropic phase boundary indicates that the physical origin of the higher piezoelectric activity is associated with higher density of non-180° domain walls. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2120909]

Using higher-frequency broadband ultrasonic transducers can lead to better axial and lateral resolutions in medical ultrasonic imaging. The design of high-frequency transducers requires better knowledge of material properties at high frequencies since the ultrasonic dispersion becomes important for frequencies above 50 MHz.[1] The dispersion of velocity and attenuation may also deform the acoustic pulse causing inappropriate interpretation of the ultrasonic signals. Therefore, knowing the properties of transducer materials at high-frequencies not only helps in the simulation and design of high frequency transducers but also helps in the analysis of pulse signals in imaging processing.

Although lead zirconic titanate (PZT) ceramics have been the dominant ultrasonic transducer materials in the past 40 years, they exhibit high attenuation and significant velocity dispersion at high frequencies due to the strong scattering of acoustic waves at the grain boundaries and the presence of pores in the ceramics. Therefore, for frequencies above 30 MHz, single crystals, such as $LiNbO_3$ and quartz, are usually used for making ultrasonic transducers. However, the electromechanical coupling coefficients and piezoelectric coefficients of these single crystals are too low to produce broadband transducers with good sensitivity, which affects the penetration depth and the imaging quality.

Recently, relaxor-based single crystals $(1-x)Pb(Zn_{1/3}Nb_{2/3}-xPbTiO_3$ (PZN-PT) and $(1-x)Pb(Mg_{1/3}Nb_{2/3})-xPbTiO_3$ (PMN-PT) have been studied extensively and it was found that the piezoelectric coefficient $d_{33}$ of [001]-poled PZN-PT and PMN-PT crystals can reach 2900 pC/N and the electromechanical coupling coefficient $k_{33}$ is greater than 90% for compositions near the morphotropic phase boundary (MPB).[2–5] The high coupling coefficient and large piezoelectric coefficient are very attractive for producing ultrasonic transducers with higher sensitivity and superior broadband characteristics, actuators with larger strains and low power consumption, and many other more efficient electromechanical devices.

The superior electromechanical properties only occur in single crystals with multiple-domain structures, which are produced by poling single crystals along [001] or [110] of the cubic coordinates while the true dipolar direction is in ⟨111⟩ families so that the true single-domain crystal symmetry is rhombohedral $3m$. Since the ultrasonic attenuation is closely associated with the presence of domain walls, it is important to know whether the attenuation and velocity dispersion of these multidomain crystals are still comparable to other single-domain single crystals.

It was demonstrated that the attenuation of PMN-28%PT at high frequencies is much lower than that of the PZT ceramics.[6] However, the piezoelectric properties of the PMN-28%PT crystal are not the best in this solid solution system since the composition is away from the MPB, which is PMN-33%PT at room temperature.[7] In this paper, we report the dispersion measurements for the longitudinal wave propagating in PMN-32%PT single crystal, which is much closer to the MPB but still on the rhombohedral phase side. The reason not to directly measure the MPB composition is because the properties of the MPB composition are not as stable and there are often tetragonal phases present in the MPB composition crystals.

The PMN-32%PT crystals used in this work were grown by the JFE Mineral Co., Ltd. of Japan using a modified Bridgman method. After the crystallographic orientations were determined using a DX-4 x-ray single-crystal orientation unit with an accuracy of ±0.5°, the crystals were cut into plates with the dimensions of $20\times20\times0.5$ mm$^3$ with orientations of [100]/[010]/[001] and [110]/[$\bar{1}$10]/[001], respectively. The square planes of $20\times20$ mm$^2$ are (001) and (110) faces, respectively. Poling was performed by applying a 6 kV/cm electrical field along the thickness direction at 23 °C after sputtering Pd and Au electrode layers on both basal planes with the thickness of 0.05 and 0.45 $\mu$m, respectively. For the [001]-poled specimen, test on a modified Berlincourt-type meter gives $d_{33}\sim2100$ pC/N, and impedance measurements give the coupling coefficient $k_{33}$=92%, free dielectric constant $\varepsilon_{33}^T$=7300, and tan $\delta<0.3\%$ at

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0003-6951/2005/87(18)/182903/3/$22.50

1 kHz. For the [110]-poled crystals, the piezoelectric constant $d_{33}$=900 pC/N, electromechanical coupling coefficient $k_{33}$=70%, and free dielectric constant $\varepsilon_{33}^T$=4000 have been obtained.

The ultrasonic spectra of longitudinal wave propagating in PMN-32%PT single crystals were measured by through-transmission method using the experimental setup described in Ref. 1. A pair of immersion-type transducers with center frequency of 100 MHz (E9934, Valpey-Fisher, Hopkinton, MA) was aligned inside a water tank. The transmitting transducer was driven by a pulser/receiver (5900 PR, Panametrics, Waltham, MA). The transmitted signal was detected by the receiving transducer in two different situations: one case is with only water in between the transducers and the other is with sample in between the transducers. The received time domain signals were recorded by a digital oscilloscope (TDS 430A Tektronix), then downloaded to a computer where the fast Fourier transform (FFT) of the time domain signals was performed. The frequency dispersion of attenuation $\alpha(f)$ and the slowness $u(f)=1/V(f)$ can be obtained from the following formula:[1]

$$\alpha(f) = \alpha_W(f) + \ln\left[T\frac{A_W(f)}{A_S(f)}\right]/d, \tag{1}$$

$$u(f) = \frac{1}{V_S(f_0)} - \frac{1}{V_S(f)} = \frac{[\varphi_W(f_0) - \varphi_S(f_0)]}{2\pi f_0 d} - \frac{[\varphi_W(f) - \varphi_S(f)]}{2\pi f d}, \tag{2}$$

where $A$ and $\Phi$ represent the amplitude and phase spectra of the received signals, respectively. The subscripts $W$ and $S$ stand for water and the sample, respectively, $f_0$ is a reference frequency chosen inside the bandwidth of the transducers, $V_s(f)$ is the wave velocity in the sample at frequency $f$, $d$ is the sample thickness, and $T$ is the total transmission coefficient for the ultrasonic wave to pass through the sample (or from sample to water). Although the crystal symmetry is rhombohedral $3m$, the multidomain crystal poled along [001] has a macroscopic symmetry of tetragonal $4mm$, while the multidomain crystal poled along [110] has a macroscopic symmetry of orthorhombic $mm2$. The longitudinal wave propagating along the poling direction of both samples are pure-mode waves, therefore, the transmission coefficient $T$ can be calculated by

$$T = \frac{4\rho_S\rho_W V_S V_W}{(\rho_S V_S + \rho_W V_W)^2}, \tag{3}$$

for the normal incident ultrasonic wave.[1] In Eq. (3), $\rho_S$(=8050 kg/m$^3$) and $\rho_W$ are the mass densities of the sample and water, respectively, and $V_w$ is the wave velocity in water.

The velocity in the sample at the reference frequency $f_0$=50 MHz was measured directly using the conventional pulse-echo method.[8] The velocity dispersion is then derived from[1]

$$V(f) = \frac{V(f_0)}{1 - u(f)V(f_0)}. \tag{4}$$

The measured frequency dependence of the attenuation and slowness of ultrasonic waves in PMN-32%PT single crystal are shown in Figs. 1 and 2, respectively. For comparison, the data for PZT-4 ceramic sample (Valpey-Fisher, Hopkinton, MA) and a $z$-cut single-crystal $LiNbO_3$ sample (Valpey-Fisher, Hopkinton, MA) are also shown in Figs. 1 and 2.[6] It was observed that the attenuation and velocity dispersion of PMN-32%PT single crystal poled along [110] of cubic axis are a little smaller than those of [001]-poled PMN-32%PT single crystal. Again, similar to the conclusion of Ref. 6, the dispersions of velocity and attenuation in both crystals are smaller than those of PZT-4, which has the lowest attenuation in the family of PZT ceramics. However, both crystals measured here exhibit much higher attenuation and velocity dispersion than those reported for PMN-28%PT crystal.[6]

Our measured results show that the domain patterns become more attenuative for high-frequency waves as the PMN-PT composition is getting closer to the MPB composition. Because the ultrasonic attenuation in single crystals is mainly caused by the wave scattering from domain

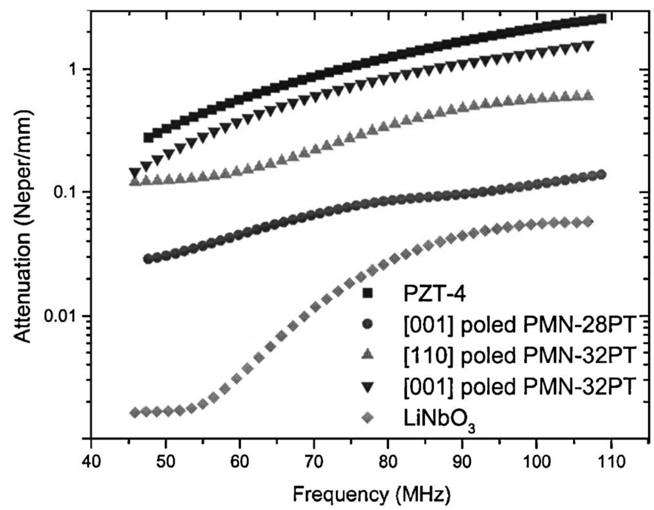


FIG. 1. Frequency dependence of ultrasonic attenuation of the longitudinal wave along the poling direction for [001]- and [110]-poled PMN-32%PT single crystals. For comparison, the attenuation dispersions for [001]-poled PMN-28%PT single crystal, PZT-4 ceramic, and $LiNO_3$ single crystal are also provided.

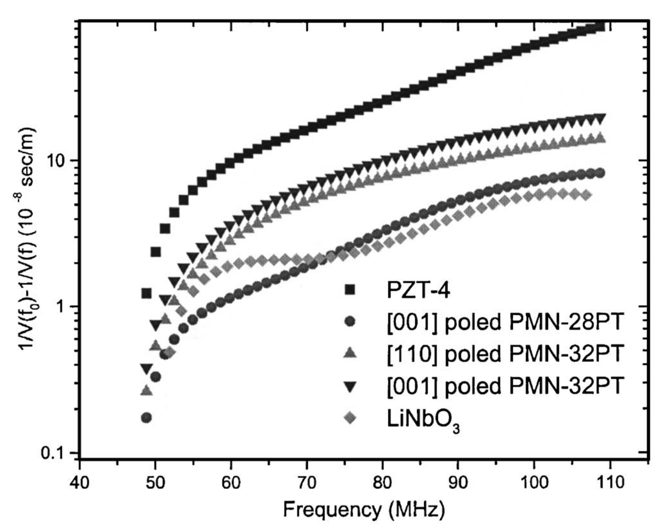


FIG. 2. Frequency dispersion of the slowness of the longitudinal wave in the poling direction for [001]- and [110]-poled PMN-32%PT single crystals. For comparison, the dispersions of slowness in [001]-poled PMN-28%PT single crystal, PZT-4 ceramic, and $LiNO_3$ single crystal are also given.

boundaries[9] and poling had eliminated 180° domain walls, the correlation between high piezoelectric activity and high attenuation implies that non-180° domain-wall density becomes higher (or the domain size is getting smaller) as the composition is getting closer to the MPB. In other words, the superior piezoelectric properties at the MPB composition are associated with finer scale and more complex domains, which produce more domain walls. These domain walls are mainly 71° and 109° types for the rhombohedral symmetry crystals investigated here. It can be envisioned that tetragonal 90° domain walls may also be produced in the MPB composition. Such increase in domain-wall density will naturally cause severe increase of ultrasonic attenuation. The experimental results provide us some important information about the MPB relation to domain structures and shed some lights on the mechanism of piezoelectric property enhancement in multidomain systems. Such information is also critical for the practical application of the PMN-PT crystals since different electromechanical devices will have different requirements for the attenuation level. The actual sensitivity and bandwidth of an ultrasonic transducer are determined not only by the piezoelectric coefficient and coupling coefficient but also by the ultrasonic attenuation.

This research was supported by the NIH under Grant No. RR11795-05. High-quality PMN-32%PT crystals used in the experiments were provided by Dr. Mitsuyoshi Matsushita of the JFE Mineral Co., Ltd. of Japan.

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