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Frequency Dispersion of Longitudinal Ultrasonic Velocity and Attenuation in [001]_c-Poled 0.24Pb(In_{1/2}Nb_{1/2})O₃–0.45Pb(Mg_{1/3}Nb_{2/3})O₃–0.31PbTiO₃ Single Crystal

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Abstract

The frequency dispersion of ultrasonic velocity and attenuation in [001]_c-poled 0.24Pb(In_{1/2}Nb_{1/2})O₃–0.45Pb(Mg_{1/3}Nb_{2/3})O₃–0.31PbTiO₃ (PIN-0.45PMN-0.31PT) ternary single crystal were measured by ultrasonic spectroscopy from 25 to 100 MHz for the longitudinal wave. It was found that the velocity has a linear relationship with the frequency f , but the attenuation has a quadratic relation with f . The attenuation and frequency dispersion of the ternary system are lower than that of the (1– x)Pb(Mg_{1/3}Nb_{2/3})O₃– x PbTiO₃ (PMN-PT) binary system and the coercive field also increased by a factor of 2.5, hence, the ternary single system is superior to the corresponding binary single-crystal system for high-frequency and high-power transducer applications.

I. Introduction

High-frequency broadband ultrasonic transducers have attracted more and more attention in medical imaging because of the increasing demand for better axial and lateral resolutions [1], [2]. The core element in an ultrasonic transducer is the piezoelectric resonator, which can transform electric energy into mechanical waves that propagate into target tissues and reflect from internal structures to form an image. In the past 50 years, the dominant active piezoelectric material for ultrasonic transducers is lead zirconic titanate (PZT) ceramic, which has high attenuation and noticeable velocity dispersion at high frequencies because of the strong scattering of acoustic waves at the grain boundaries [3].

Recently, it was demonstrated that the attenuation of relaxor-based ferroelectric single crystals (1– x) Pb(Mg_{1/3}Nb_{2/3})O₃– x PbTiO₃ (PMN-PT), which have superior electromechanical properties [4], [5], is much lower than that of PZT ceramic at high frequencies [6], [7]. Zhou *et al.* had fabricated high-frequency ultrasonic needle transducers with a center frequency of 44 MHz and –6-dB fractional bandwidth of 45% for pulsed-wave Doppler and imaging applications using PMN-PT single crystals [8]. However, this binary single crystal system has limited operating temperature because of the relatively low rhombohedral-tetragonal phase transition temperature T_{RT} (~75 to 95°C). In addition, the coercive field E_C (~2.5 kV/cm) of PMN-PT is too low for high-field applications, and its performance often degrades when being integrated into device assemblies. For high-frequency transducer applications, better piezoelectric crystals with electromechanical properties similar to those of PMN-PT single crystals, but with higher coercive field and higher phase transition temperatures, has been one of the main topics in piezoelectric materials research in recent years.

The ternary single-crystal system $x\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-(1-x-y)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-y\text{PbTiO}_3$ (PIN-PMN-PT) was found to possess such desired properties. They have electromechanical properties similar to those of PMN-PT single crystals, but the rhombohedral-tetragonal phase transition temperatures are about 30°C higher and the coercive field is increased by a factor of 2.5 [9]–[12]. More recently, Sun *et al.* have designed and fabricated high-frequency ultrasonic transducers using PIN-PMN-PT single crystal with center frequencies of 35 and 60 MHz. Their results showed that the PIN-PMN-PT single-crystal transducers have similar performance to, but much better thermal stability than, transducers made of PMN-PT single crystals [13]. For the design optimization of high-frequency transducers, it is critical to know the dispersion of velocity and attenuation at high frequencies, but such data are still lacking.

In this paper, we report the measured frequency dispersion of longitudinal wave velocity and attenuation for waves propagating along the poling direction $[001]_c$ in a $0.24\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-0.45\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.31\text{PbTiO}_3$ (PIN-0.45PMN-0.31PT) single crystal in the frequency range of 25 to 100 MHz. Our results revealed the frequency dependence of the acoustic properties, which can be used as input for the finite-element design of high-frequency ultrasonic transducers.

II. Experimental Procedure

The PIN-0.45PMN-0.31PT single crystal used in this work was grown by a modified Bridgman method [10]. The as-grown single crystal was oriented by a Laue X-ray machine and cut into a thin plate with the dimensions of $25.4 \times 25.4 \times 0.542$ mm oriented along $[001]_c$. The thin plate was polished and sputtered with gold electrodes on the large surfaces, then poled by a 10-kV/cm electric field at room temperature. After being poled along $[001]_c$ of the pseudocubic direction, the multi-domain structure has a macroscopic tetragonal 4 mm symmetry. The density ρ (8179 kg/m³) was determined by the Archimedes's principle, and the piezoelectric constant d_{33} (1763 pC/N) was directly measured by using a ZJ-2 piezo meter (Institute of Acoustics, Chinese Academy of Sciences, Beijing, China), and the d_{33} is similar to that of the $[001]_c$ -poled PMN-0.30PT single crystal ($d_{33} = 1760$ pC/N) [14]. The stress-free dielectric constant $\epsilon_{33}^T/\epsilon_0$ (5496), dielectric loss $\tan \delta$ (0.8%), electromechanical coupling factor k_t (0.58), elastic stiffness constant c_{33}^E (10.85×10^{10} N/m²), and c_{33}^D (16.35×10^{10} N/m²) were obtained by the resonance technique using an HP 4194A impedance-phase gain analyzer (Agilent Technologies, Santa Clara, CA).

The frequency dispersions of ultrasonic velocity and attenuation were measured using the ultrasonic spectroscopy technique we have developed [3]. The experimental setup is shown in Fig. 1. Two immersion-type transducers were aligned properly in a water tank filled with deionized water. One was used as the transmitter and the other was used as the receiver. The distance between the two transducers is ~3 cm. To obtain the dispersions from 25 to 100 MHz, two pairs of immersion-type broadband transducers with center frequencies of 50 and 100 MHz were used. The transmitting transducer was driven by a 200-MHz pulser/receiver (5900PR, Panametrics, Waltham, MA). One computer-controlled rotation table rotates the sample to change the angle of incidence. The angle resolution of our setup is 0.01°.

The longitudinal wave was normally incident upon the plate sample, and the transmitted signals for cases without and with the sample between the transducers were received, amplified, and recorded by a digital oscilloscope (TDS 460A, Tektronix, Beaverton, OR) at a sampling rate of 10 G sample/s. The total sampling length for each waveform was 2500 points and each waveform was transferred to a personal computer via a GPIB interface for data processing. To reduce random errors, each signal was averaged 64 times. During signal processing, the time-domain signals were converted into frequency-domain data via fast

Fourier transform (FFT); then, the frequency-dependent phase velocity and attenuation can be calculated accordingly. The received pulse signals together with their FFT for cases without and with the sample between the transducers are shown in Fig. 2 (measured by 50-MHz transducers) and Fig. 3 (measured by 100-MHz transducers).

The phase velocity v_L and the attenuation α_L of the longitudinal wave were calculated using the following equations [3]:

$$v_L = \frac{v_w}{1 + \frac{(\varphi_s - \varphi_w + 2\pi f\tau)v_w}{2\pi fd}}, \quad (1)$$

$$\alpha_L = \alpha_w + \ln\left(\frac{T_L A_w}{A_s}\right)/d, \quad (2)$$

where v_w is the acoustic velocity in water (1480 m/s at 20°C), α_w is the attenuation of water, f is the frequency, τ is the delay time between the two time windows used to acquire the signals for cases with and without the sample in the acoustic pathway, d is the thickness of the sample, and T_L is the transmission coefficient for the longitudinal wave through the sample, i.e.,

$$T_L = \frac{4\rho_w v_w \rho_s v_L}{(\rho_w v_w + \rho_s v_L)^2}, \quad (3)$$

where ρ_w and ρ_s are the densities of water and the sample, respectively.

III. Results and Discussion

The measured frequency dependence of phase velocity and attenuation for the longitudinal wave in [001]_c-poled PIN-0.45PMN-0.31PT single crystal are shown in Fig. 4. To ensure the reliability of the measured data, we have performed detailed error analysis. If a quantity $q = f(x_1, x_2, \dots)$ is a function of some quantities $x_1, x_2, \dots$, with errors $\delta x_1, \delta x_2, \dots$, then the error of q can be expressed as $\Delta q = \sum_j \left| \frac{\partial f}{\partial x_j} \right| \delta x_j$ [15]. We estimated that the relative errors of phase velocity and attenuation are about 0.48% and 3.53%, respectively, as shown in Fig. 4. The error bars specify the error limit.

From the measured data, the longitudinal phase velocity only changed about 0.4% from 25 to 100 MHz. On the other hand, the attenuation increased rapidly with frequency, but its magnitude is still relatively small compared with other known piezoelectric materials. In fact, the attenuation coefficient of the [001]_c-poled PIN-0.45PMN-0.31PT (0.59 N p/mm) is only about 40% of that of [001]_c-poled PMN-0.32PT (1.40 Np/mm) at 100 MHz, and much lower than the attenuation coefficient of PZT-4 (2.17 N p/mm), which has the lowest attenuation in the family of PZT ceramics [6], [7]. The ultrasonic attenuation in PMN-PT or PIN-PMN-PT is mainly caused by the wave scattering from domain walls because of the multi-domain structure in these crystals.

It is known that the dispersions of velocity and attenuation are correlated through the Kramers-Kronig relationship [16]. Therefore, the phase velocity dispersion can be derived from the measured frequency-dependent attenuation and vice versa. The approximate nearly local relationship is given by

$$v(\omega) = v(\omega_0) + \frac{2v^2(\omega_0)}{\pi} \int_{\omega_0}^{\omega} \frac{\alpha(\omega)}{\omega^2} d\omega \quad (4a)$$

$$\alpha(\omega) = \frac{\pi\omega^2}{2v^2(\omega_0)} \frac{dv(\omega)}{d\omega}, \quad (4b)$$

where ω_0 is the starting angular frequency and $v(\omega_0)$ is the sound velocity at ω_0 .

For most materials, the attenuation obeys the power-law frequency dependence: $\alpha = a \cdot f^b$, where a and b are two material-dependent parameters, with $1 \leq b \leq 2$ [17], [18]. The velocity dispersion and attenuation derived from the Kramers-Kronig relationship are plotted in Fig. 4, together with the experimental data. We can see that the derived curves reasonably agree with the measured ones. The small difference between the experimental data and the Kramers-Kronig relations is mainly caused by the nonlinear nature of the material, because the Kramers-Kronig relations are valid only for linear media. From the experimental data, the frequency dependence of phase velocity v_L (in meters per second) and attenuation α_L (in nepers per millimeter) may be fitted into the following relations:

$$v_L = 4480 + 0.126f \quad (5a)$$

$$\alpha_L = 6.185 \times 10^{-5} f^2. \quad (5b)$$

where the frequency is expressed in megahertz.

From (5a) and (5b), we can see that the velocity has a linear relationship with the frequency f , whereas the attenuation has quadratic relation with f in the high-frequency range. These mathematical expressions, (5a) and (5b), may be used for the finite element design of high-frequency ultrasonic transducers.

Based on the Christoffel wave equation, the phase velocity of a longitudinal wave propagating along the poling direction $[001]_c$ is connected with the elastic stiffness constant $c_{33}^D = \rho v^2$. When the attenuation is taken into account, the elastic stiffness constant becomes a complex number: $c_{33}^D = c' + jc''$. The complex wave number may be expressed as

$$\tilde{k} = k - j\alpha, \quad (6)$$

where $k = \omega/v$ and α is the attenuation coefficient. Thus, the real and imaginary parts of the elastic stiffness constant are related to the measured phase velocity and attenuation through [3]

$$c' = \rho v^2 \quad (7a)$$

$$c'' = \frac{\rho v^3 \alpha}{\pi f}. \quad (7b)$$

From the measured frequency dependence of phase velocity and attenuation, the real and imaginary parts of the elastic stiffened constant c_{33}^D were also calculated as shown in Fig. 5, with estimated error bars. The relative errors of c' and c'' were calculated to be 1.01% and

5.02%, respectively. The errors are a little larger than that of phase velocity and attenuation because of the error propagation. From Fig. 5, we can see that the dispersion of the real part of the elastic stiffened constant is very small, similar to the dispersion of velocity. But the imaginary part of the elastic constant has very strong frequency dependence.

IV. Summary and Conclusion

The frequency dependence of ultrasonic velocity and attenuation for the longitudinal wave propagating along the poling direction $[001]_c$ in a PIN-0.45PMN-0.31PT single crystal with engineered domain structure are measured in a wide frequency range from 25 to 100 MHz by using ultrasonic spectroscopy. The velocity has a linear relationship with the frequency f , whereas the attenuation has quadratic relation with f in the frequency range studied. The multi-domain single crystal exhibited very low attenuation, even at 100 MHz, and the velocity dispersion is only about 0.4% up to 100 MHz. Compared with PMN-PT single crystals, such low dispersion and low attenuation plus larger coercive field and higher phase transition temperatures make the PIN-PMN-PT single crystals much better candidates for applications in high-drive, high-temperature, and high-frequency ultrasonic transducers.

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Biographies

Enwei Sun was born in 1983 in Shandong, China. He received the B.S. degree in physics from Yantai Normal University, Yantai, China, in 2005, and the M.S. degree in condensed matter physics from the Harbin Institute of Technology, Harbin, China, in 2007.

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Wenwu Cao received his B.S. degree in physics from Jilin University in 1982, and his Ph.D. degree in condensed matter physics from The Pennsylvania State University in 1987.

He is a Professor of Mathematics and Materials Science, a joint appointment between the Department of Mathematics and the Materials Research Institute of The Pennsylvania State University. He has conducted both theoretical and experimental research in the fields of condensed matter physics and materials science, including theories on proper- and improper-ferroelastic phase transitions, static and dynamic properties of domains and domain walls in

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Pengdi Han (M'90), one of the pioneers in crystal growth by the large-scale multicrucible Bridgman method, is the founder of H. C. Materials Corporation in Bolingbrook, IL. After being awarded his B.Sc. degree in electrical engineering (1964) from Wuhan University of Technology, he joined the crystal growth group of synthetic fluorine mica at the Shanghai Ceramic Institute, China. He became a research associate in the Research Institute of Synthetic Crystals at Beijing, China, after accomplishment of graduate studies in theory of crystal growth in the Chemistry Department of Shandong University, China (1978). He was awarded three Outstanding Researcher Prizes by the State Science Committee of China. He served as the Director of Department of Functional Crystals and member of the Scientific Committee in the Research Institute of Synthetic Crystals (1979–1986). He joined Professor David Payne's group as a Senior Research Scientist at the University of Illinois at Urbana-Champaign, Urbana, IL (1987–2000). His research interests include crystal growth and crystal physics. He has authored more than 120 papers, one book, and three patents.

Fig. 1.
Experimental setup.

Fig. 2.
The (a) received pulse signals and (b) FFT for cases without and with the sample between the transducers, measured by 50-MHz transducers.

Fig. 3.
The (a) received pulse signals and (b) FFT for cases without and with the sample between the transducers, measured by 100-MHz transducers.

Fig. 4.

The frequency dispersion of the phase velocity and attenuation of the longitudinal wave in a [001]_c-poled PIN-0.45PMN-0.31PT single crystal.

Fig. 5.

The frequency dispersion of the real and imaginary parts of the elastic stiffness constant c_{33}^D of a $[001]_c$ -poled PIN-0.45PMN-0.31PT single crystal.