Electromechanical Properties of Fine-Grain, 0.7 $Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$ Ceramics

Haifeng Wang, Bei Jiang, Thomas R. Shrout, and Wenwu Cao

***Abstract*—A fine grain, relaxor-based piezoelectric ceramic 0.7 $Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$ (PMN-30% PT) has been investigated, which was fabricated using the columbite precursor method. The complete set of electromechanical properties of the piezoceramic at room temperature is determined using a combination of ultrasonic and resonance techniques. This fine-grain ceramic (grain size $\leq$ 2.5 μm) exhibits ultra-high dielectric permittivity ($\varepsilon_{33}^T/\varepsilon_0 \sim 7000$) and a high coupling coefficient k_{33} ($= 0.78$). Ultrasonic spectroscopy was used to measure the dispersion of the phase velocity and attenuation for the longitudinal wave propagating in the poling direction. Lower attenuation and smaller velocity dispersion were observed compared to modified $Pb(Zr_xTi_{1-x})O_3$ (PZT-5H) ceramics. The measurement results show that this fine-grain PMN-30% PT ceramic is a very good material for making ultrasonic array transducers.**

I. Introduction

With the ability of dynamic focusing and beam steering in the azimuth and elevation directions, two-dimensional (2-D) phased arrays can further improve the quality of clinical ultrasound images [1]–[3]. However, a typical modified $Pb(Zr_xTi_{1-x})O_3$ (PZT-5H) ceramic array element has a clamped capacitance of about 4 pF with an electrical impedance of about 10 kΩ at 2.5 MHz due to the small size and large aspect ratio of the element. The large electrical impedance mismatch between the array elements and the 50 ohm imaging electronics greatly reduces the signal-to-noise ratio (SNR). Although transformers theoretically can be used to bridge the mismatch, additional factors (such as thermal effects, packing considerations, etc.) limit the tuning ability of inductors.

Multilayer elements using stacked ceramic plates technology [4], [5] has been investigated as a way of increasing element capacitance. However, these methods only achieved limited success due to the complexity in fabricating and interconnecting multilayer elements in the form of 1–3 composites [4]. A simpler method is to use materials with a high dielectric constant because the array element possesses electrical impedance inversely proportional to the dielectric constant of the piezoelectric material. Kong *et al.* [6] have prepared the fine grain, translucent PMN-PT ceramics. But they did not report the electromechanical properties. They also added excessive PbO, which is detrimental to dielectric properties.

In this work, a fine grain, relaxor-based piezoelectric ceramic 0.7 $Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$ (PMN-30% PT) was developed specifically for medical ultrasound array applications with a dielectric permittivity significantly higher than that of PZT-5H. Our investigation includes characterizations of the complete set of electromechanical properties and frequency spectrum of the ultrasonic attenuation.

For a poled piezoceramic, there are 10 independent material constants: 5 elastic constants, 3 piezoelectric coefficients, and 2 dielectric permittivities. A combined ultrasonic-resonance technique has proven to be effective for the determination of the complete set of electromechanical properties of piezoelectric materials [7]–[10].

Ultrasonic spectroscopy was used here to study the frequency dispersions of phase velocity and attenuation of the longitudinal wave propagating in the poling direction. It was found that the fine grain PMN-30% PT ceramic exhibits low attenuation and small velocity dispersion in the measured frequency range. Most importantly, compared to the commonly used PZT-5H ceramics, a two-fold increase in the dielectric constant ε_{33} was observed, but the coupling coefficient k_{33} is about the same. These good qualities make the PMN-30% PT ceramic an ideal material for fabricating 2-D ultrasonic imaging arrays.

II. Materials and Characterization Methods

Fine grain piezoelectric ceramic of the (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ family with x = 0.3 (TRS Ceramics, State College, PA) was synthesized following the work of Choi *et al.* [11]. Loss on ignition test was performed on all starting materials to ensure proper stoichiometry. The columbite precursor method was used, whereby Nb_2O_5 and $MgCO_3$ were mixed in the reaction $MgO + Nb_2O_5 \Rightarrow MgNb_2O_6$ and calcined at 1200°C for 4 hours. X-ray diffraction (XRD) patterns confirmed single-phase columbite formation. Before adding PbO and TiO_2, the columbite powder was dry-milled and passed through a 100 mesh sieve, then made into a slurry and put into a high-energy attritor-mill for 6 hours.

PbO, in the form of $PbCO_3$, and TiO_2 were mixed with the columbite and vibratory-milled in pH-adjusted DI H_2O and dispersant for 18 hours. The slurry was dried then calcined at 700°C for 4 hours. The XRD patterns confirmed

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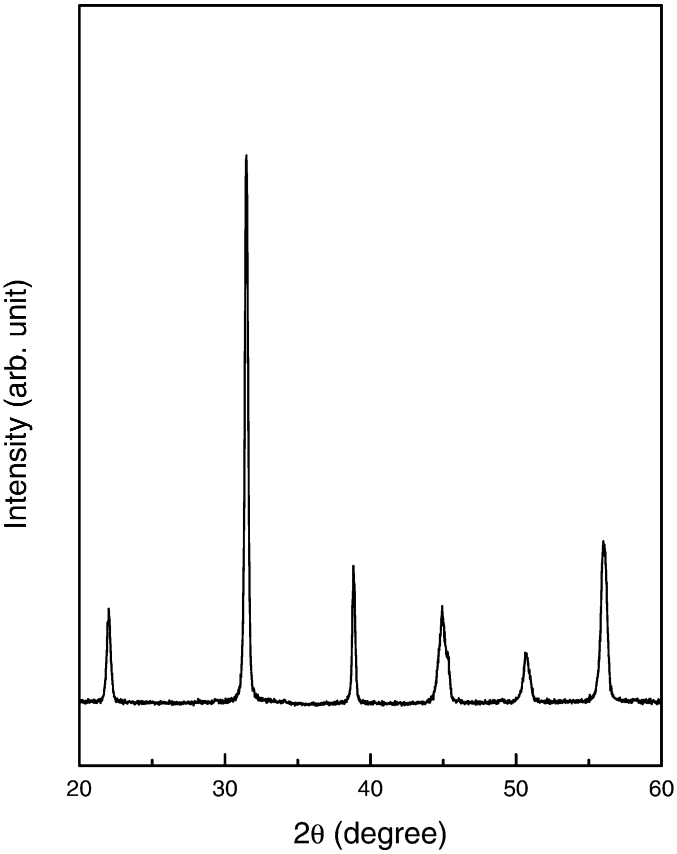

Fig. 1. XRD diffraction pattern of PMN-30% PT ceramic sample.

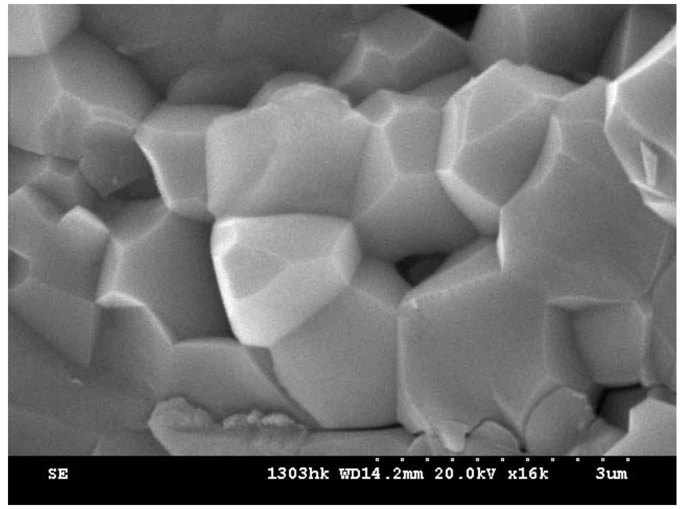

Fig. 2. SEM micrograph of PMN-30% PT ceramic sample.

a nearly phase-pure perovskite structure with about 2% pyrochlore phase. This powder was ground using a mortar and pestle, passed through 80 mesh, then attritor-milled for 8 hours to obtain a submicro powder and subsequent fine-grain microstructure.

Acrylic resin binder was added to the powder and granulated in order to maintain strength for pressing. Blocks with dimensions 76 mm $\times$ 50 mm $\times$ 50 mm were pressed using biaxial pressure. The heating rate for binder burnout was 0.5°C/minute up to 325°C. To remove any residual carbon, the burnout cycle was taken to 550°C for 90 minutes. The ceramic bodies were fired at 1250°C for 3 hours in an Alumina crucible with $PbZrO_3$ source powder to maintain a PbO atmosphere. The sintered material was found to be phase pure perovskite determined by XRD on ground powder (Fig. 1). After sintering, the blocks were hot isostatically pressed (H.I.P.) at 1150°C for 2 hours in an O_2/Ar atmosphere to eliminate any porosity. Scanning electron microscope (SEM) measurements revealed a 2.5-μm grain size (Fig. 2), which is smaller than the value observed in commercial PZT ceramics ($\sim$5 μm). The density was found to be 8.00 g/cm^3, which is 99% of theoretical value.

Four specimens were cut and lapped to proper dimensions for property measurements: a rectangular parallelepiped with one surface normal to the poling direction, a square plate with its major surface normal to the poling direction (k_t plate), a bar with its length along poling direction (k_{33} bar); and a bar with its length normal to the poling direction (k_{31} bar). All specimens were poled under a field of 2 kV/mm for 10 minutes at 60°C. Tests with higher fields indicated that these conditions fully poled the specimens.

The pulse-echo method was used for the ultrasonic measurements, in which a 15-MHz longitudinal wave transducer (Ultran Laboratories, Inc., Boalsburg, PA) and a 20-MHz shear wave transducer (Panametrics, Waltham, MA) were used to determine the velocity of longitudinal and shear waves, respectively. The transducers were excited by a Panametrics 200 MHz pulser/receiver, and the time of flight between echoes was determined by a Tektronix 460A (Tektronix, Inc., Beaverton, OR) digital oscilloscope. The resonance method described in the IEEE standards [15] was performed using a HP 4194A Impedance/Gain-phase (Hewlett-Packard, Palo Alto, CA) analyzer. The resonance and antiresonance frequencies, corresponding to the minimum and maximum values of the impedance-frequency spectrum, were used to calculate the corresponding electromechanical coupling coefficients and elastic compliances. The dielectric measurements were carried out at 1 kHz using a Stanford Research System SR715 LCR Meter (Stanford Research Systems, Inc., Sunnyvale, CA).

The experimental setup for the through-transmission ultrasonic spectroscopy was described in [12]. Two immersion-type broadband transducers (Panamatrix V358, Panametrics, Waltham, MA) with center frequency of 50 MHz were used. The transmitting transducer was driven by a Panametrics 200-MHz pulser. The signals from the receiving transducer, for the cases of without and with sample in between the transducers, were recorded using a Tektronix TDS 460A digital oscilloscope, and transferred to a personal computer where the fast Fourier transform (FFT) is performed. The dispersion of the phase velocity and attenuation can be obtained from [13]:

$$\frac{1}{v(\omega_0)} - \frac{1}{v(\omega)} = \frac{\varphi_w(\omega_0) - \varphi_s(\omega_0)}{\omega d} - \frac{\varphi_w(\omega) - \varphi_s(\omega)}{\omega_0 d}, \quad (1)$$

and

$$\alpha = \alpha_w + \ln\left(\frac{TA_w}{A_s}\right)/d, \quad (2)$$

where A and φ represent amplitude and phase spectra of the detected signals, respectively; ω_0 is a reference frequency chosen inside the bandwidth of the transducers; and d is the sample thickness. The subscripts w and s stand for the spectra of the signals without and with the sample in between the transducers, respectively. T is the total transmission coefficient given by:

$$T = \frac{4\rho_w v_w \rho v}{(\rho_w v_w + \rho v)^2}. \quad (3)$$

where ρ_w and ρ are mass density of water and sample, and v_w is the wave velocity in water.

III. Results and Discussion

The phase velocity of longitudinal and shear waves along and perpendicular to the poling direction of sample 1 were measured using the pulse-echo method. Five corresponding elastic constants c_{11}^E, c_{33}^D, c_{44}^E, c_{44}^D, and c_{66}^E were determined from these measurements. The resonance and antiresonance frequencies of samples 2–4 were measured, and the following material constants were determined: k_t, k_{33}, k_{31}, s_{11}^E, and s_{33}^D. A Berlincourt d_{33} meter (Academia Sinica, Beijing, PR China) was used to measure the piezoelectric coefficient d_{33} directly, and the dielectric constants ε_{11}^T and ε_{33}^T were obtained from capacitance measurements. The complete set of elastic, piezoelectric, and dielectric constants of the PMN-30% PT ceramic is listed in Table I. The independent material constants marked with a star (*) in Table I were measured directly, but the other constants in Table I were derived using constitutive relations. The dielectric loss tangent of ε_{11}^T and ε_{33}^T are both 0.02.

The results show that fine-grain PMN-30% PT ceramics have a very high dielectric permittivity with $\varepsilon_{33}^T/\varepsilon_0 \sim 7000$, which is twice that of PZT-5H ($\varepsilon_{33}^T/\varepsilon_0$ around 3400 [14]). Because the electrical impedance of the array element is inversely proportional to the dielectric constant of the piezoelectric materials, the fine-grain PMN-30% PT ceramic will have better electrical matching with the imaging electronics. Meanwhile, the coupling coefficient k_{33} ($\sim$0.78), which plays an important role in 2-D arrays, is about the same as that of PZT-5H ($k_{33} \sim 0.75$). Therefore, a better SNR of the arrays can be expected by using the novel PMN-30% PT ceramic.

The elastic constants of fine grain PMN-30% PT ceramic are close to those of PZT-5H. The piezoelectric constant d_{33} of PMN-30% PT ceramic is larger than that of PZT-5H, which can result in better transmitting efficiency.

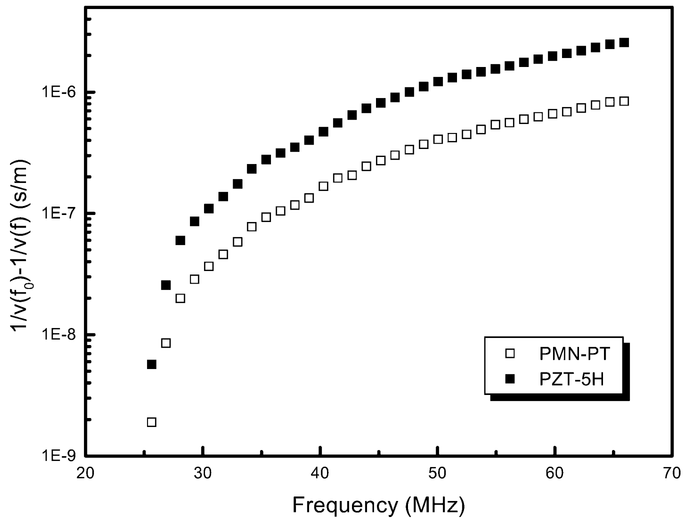

Fig. 3. The dispersion of phase velocity of PMN-30% PT and PZT-5H ceramics.

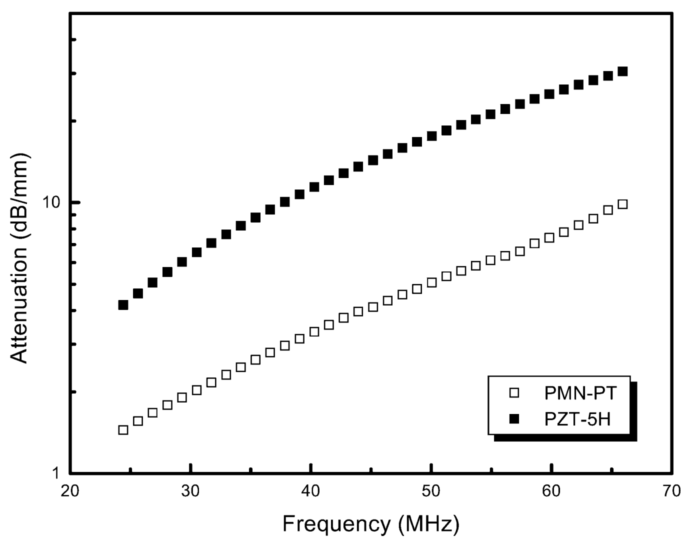

Fig. 4. The attenuation in PMN-30% PT and PZT-5H ceramics.

The dispersion of phase velocity and attenuation of the longitudinal wave in the poling direction were also measured using sample 1 by the ultrasonic spectroscopy. The results in the frequency range from 25 MHz to 65 MHz are shown in Figs. 3 and 4, respectively. As a comparison, the measured results for the PZT-5H piezoceramic are also shown in these figures. One can see that the fine-grain PMN-30% PT ceramic has lower attenuation and smaller dispersion of phase velocity, making it a better candidate for the high-frequency array applications.

IV. Conclusions

In this paper, a fine-grain, relaxor-based piezoelectric ceramic 0.7 $Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$ was investigated. By using both ultrasonic and resonance techniques, the complete electromechanical properties of this material

TABLE I
Material Constants of PMN-30%PT Fine-Grain High Dielectric Constant Ceramic.

Elastic constants c_{ij} (10^{10} N/m^2)											
c_{11}^{E*}	c_{12}^{E}	c_{13}^{E}	c_{33}^{E}	c_{44}^{E*}	c_{66}^{E*}	c_{11}^{D}	c_{12}^{D}	c_{13}^{D}	c_{33}^{D}	c_{44}^{D*}	c_{66}^{D}
13.8	8.50	8.40	12.2	2.14	2.65	15.9	10.6	5.27	16.8	4.31	2.65
Elastic constants s_{ij} (10^{-12} m^2/N)											
s_{11}^{E*}	s_{12}^{E}	s_{13}^{E}	s_{33}^{E}	s_{44}^{E}	s_{66}^{E}	s_{11}^{D}	s_{12}^{D}	s_{13}^{D}	s_{33}^{D*}	s_{44}^{D}	s_{66}^{D}
14.1	−4.76	−6.46	17.2	46.7	37.7	11.6	−7.28	−1.35	6.80	23.2	37.7
Piezoelectric constants d_{ij} (10^{-12} C/N), e_{ij} (C/m^2), g_{ij} (10^{-3} Vm/N), h_{ij} (10^{8} V/m)											
d_{15}	d_{31}	d_{33}^{*}	e_{15}	e_{31}	e_{33}	g_{15}	g_{31}	g_{33}	h_{15}	h_{31}	H_{33}
1090	−395	800	23.2	−20.8	30.9	21.7	−6.39	12.9	9.34	−10.1	14.5
Dielectric constants ε_{ij} (ε_0), β_{ij} ($10^{-4}\varepsilon_0^{-1}$), and coupling constants k_{ij}											
ε_{11}^{T*}	ε_{33}^{T*}	ε_{11}^{S}	ε_{33}^{S}	β_{11}^{T}	β_{33}^{T}	β_{11}^{S}	β_{33}^{S}	k_{15}	k_{31}^{*}	k_{33}^{*}	k_{t}^{*}
5660	6990	2810	2330	1.77	1.43	3.56	4.29	0.71	0.42	0.78	0.53

Quantities with the * are measured directly.

were determined at room temperature. Compared to the widely used PZT-5H ceramics, the new ceramic exhibits two-fold increase in dielectric constant, which can decrease the electrical impedance of the array elements for better electrical impedance match. The coupling coefficient k_{33} is comparable to that of PZT-5H ceramics. Therefore, arrays fabricated using the new, fine-grain PMN-30% PT ceramic will have a much better SNR than that made of PZT-5H ceramics.

Ultrasonic spectroscopy was applied to study the dispersion of the phase velocity and attenuation for the longitudinal wave propagating in the poling direction. The new ceramic shows lower attenuation and smaller velocity dispersion than PZT-5H in the measured frequency range, which is another advantage of the PMN-PT ceramics for medical-array applications compared to other existing materials.

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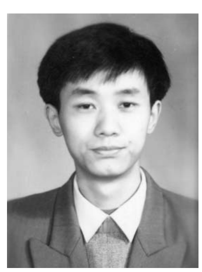

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