Determination of full set material constants of $[011]_c$ poled $0.72\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.28\text{PbTiO}_3$ single crystal from one sample

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$0.72\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.28\text{PbTiO}_3$ single crystals poled along $[011]_c$ have macroscopic orthorhombic $mm2$ symmetry. There are total 17 independent material coefficients for this symmetry so that the determination of self-consistent full matrix data is extremely difficult because many samples are needed and there is a large property variation from sample to sample. To overcome this self-consistency difficulty, we have developed a combined ultrasonic pulse-echo and impedance spectroscopy method, which can extract all coefficients from only one small sample. This method is especially useful for piezoelectric materials whose properties are strongly dependent on geometry and for crystals with only limited size available. © 2014 AIP Publishing LLC.

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In the past decade, single-crystal $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN-PT) relaxor ferroelectrics with engineered domains have attracted a growing attention due to their giant piezoelectric coefficients and ultra-high electromechanical coupling factor for compositions near the morphotropic phase boundary (MPB).^{1–5} Compared with $[001]_c$ poled single crystals, $[011]_c$ poled single crystals exhibit superior transverse and shear electromechanical properties, and they have been used in next generation transverse mode sensors and actuators.^{6,7} For device designs and fundamental studies, knowing the complete set of material properties with self-consistency is crucial. These data can greatly facilitate the use of these superior piezoelectric crystals, provide important input data for studies on the domain engineering mechanism and as input data for the modeling and design of piezoelectric devices using finite element packages.

For the characterization of full set material constants of piezoelectric materials, the most important and difficult issue is to achieve self-consistency. The complete set of material constants of $[011]_c$ poled single crystals has been reported using the resonance method.⁸ However, the data reported are lack of self-consistency, which create confusions.⁹ The cause of this problem is due to sample to sample variation because the properties of domain engineered single crystals are geometry dependent. In addition, the IEEE resonance method requires sufficient number of different geometry samples with predefined orientations. For materials with low symmetries, some geometries required for resonance measurements are difficult to obtain. Material constants that are not related to pure modes are even more difficult to obtain. In general, it is impossible to make all samples to have identical properties due to the composition inhomogeneity of the crystal boule and the geometry dependent remnant polarization. Hence, large errors will be introduced and self-consistency will be

violated. To resolve this issue, a combined ultrasonic and resonance (CUNR) method was developed and used to measure the full set material constants of $[011]_c$ poled single crystal.¹⁰ This CUNR method can eliminate unreliable modes in the resonance method and use error analysis to get self-consistency data based on the method of over-determination. Up to date, almost all material constants of PMN-PT and PZN-PT based single crystals reported in the literature were characterized by this CUNR method.^{11–16} Although this combined method reduced the number of samples compared to the IEEE resonance method, seven samples are still needed to guarantee self-consistency for the $mm2$ symmetry system. Determining all 17 independent constants using this CUNR method is laborious and a large crystal boule with uniform composition is needed to cut these samples. For many single crystals, the available sizes are usually too small to make large aspect ratio resonators and to prepare sufficient number of samples with uniform composition. There is also an intrinsic Ti segregation in the relaxor-PT single crystal systems, which prevent compositional uniformity in the whole crystal boule.

To reduce the impact of sample to sample variation on property characterization, some measurement methods have been developed using less number of samples, such as electrical impedance spectrum method,¹⁷ resonant ultrasound spectroscopy (RUS),¹⁸ and hybrid methods.^{19,20} Some were even successful to obtain all material coefficients from one sample for piezoelectric materials with 6 mm or 4 mm symmetries, which have 10 and 11 independent material constants, respectively. However, up to date, there is no report in the literature to determine the full set of material constants for $mm2$ symmetry piezoelectric crystals from one sample because there are up to 17 independent coefficients: 9 elastic constants, 5 piezoelectric constants, and 3 dielectric constants. We found that it is not possible to get enough reliable resonance peaks in the impedance spectrum to extract all 17 independent coefficients due to the strong damping at high frequencies. Although there might be enough modes in the

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FIG. 1. The coordinate system and two remaining polarization directions in $[011]_c$ poled PMN-0.28PT single crystals.

RUS method, the RUS method is inconvenient to use and it is very difficult to identify related modes when they too close to each other.¹⁸

The aim of this work is to develop a characterization method that can determine the full set material constants of $[011]_c$ poled PMN-PT single crystals from one sample with high accuracy and self-consistency. The strategy is to combine ultrasonic pulse-echo and impedance spectroscopy (CUPNIS) methods. In this method, 11 constants are determined using ultrasonic pulse-echo measurements and capacitance measurements. Especially, the lower sensitive constants for impedance spectroscopy, such as c_{55} , e_{15} , e_{24} , and e_{33}^S , are more accurately determined by direct measurements rather than the fitting regression method. With these 11 constants determined, only 6 remaining constants to be identified from the measured impedance spectrum.

The $[011]_c$ poled $0.72\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.28\text{PbTiO}_3$ (PMN-0.28PT) single crystal was grown by the modified Bridgman technique and the crystal structure is rhombohedral with 3m symmetry at room temperature. The crystal was oriented by the Laue X-ray orientation system with an accuracy of $\pm 0.5^\circ$. The sample was cut and polished into a parallelepiped with the dimensions of 5.08 mm (L) $\times$ 5.08 mm (W) $\times$ 2.60 mm (T). The sample was sputtered with gold electrodes on the pair of $[011]_c$ surfaces and poled under 5 kV/cm dc electric field in silicone oil at room temperature for 30 min. In crystals with rhombohedral symmetry, the spontaneous polarization direction in each unit cell is along one of the eight $\langle 111 \rangle_c$ directions of the pseudo-cubic coordinates. After poling, only two dipole orientations remain and the crystal shows macroscopic orthorhombic $mm2$ symmetry. The length, width, and thickness directions of the sample are along $[0\bar{1}1]_c$, $[100]_c$, and $[011]_c$, respectively. The corresponding orthorhombic coordinate system is shown in Figure 1. The poling direction $[011]_c$ is defined as axis 3, and the $[0\bar{1}1]_c$, $[100]_c$ directions are defined as axes 1 and 2, respectively. All material constant notations are based on the orthorhombic coordinate system. The density ρ of the sample was measured by the Archimedes' principle.

Ultrasonic pulse-echo method is commonly used for measuring the elastic constants of piezoelectric materials.^{21–23} Better accuracy can be achieved by ultrasonic method than resonance method.⁴ Hence, some elastic constants were first measured by the ultrasonic pulse-echo method in our experiments. A 20 MHz shear wave transducer and a 15 MHz longitudinal wave transducer were excited by a Panametrics

200 MHz pulser/receiver (Model 5900PR) for corresponding velocity measurements. A Tektronix 460 A digital oscilloscope is used to measure the time of flight between echoes. The phase velocities of the longitudinal and shear waves were measured along the three principle directions of the orthorhombic coordinate system. Eight elastic constants, c_{11}^E , c_{22}^E , c_{44}^E , c_{55}^E , c_{66}^E , c_{33}^D , c_{44}^D , and c_{55}^D , can be determined from the phase velocities of ultrasonic waves as follows:

Along direction 1:

$$c_{11}^E = (v_{1l})^2 \rho, \quad c_{66}^E = (v_{1t}^{(2)})^2 \rho, \quad c_{55}^D = (v_{1t}^{(3)})^2 \rho. \quad (1)$$

Along direction 2:

$$c_{22}^E = (v_{2l})^2 \rho, \quad c_{66}^E = (v_{2t}^{(1)})^2 \rho, \quad c_{44}^D = (v_{2t}^{(3)})^2 \rho. \quad (2)$$

Along direction 3:

$$c_{33}^D = (v_{3l})^2 \rho, \quad c_{55}^E = (v_{3t}^{(2)})^2 \rho, \quad c_{44}^E = (v_{3t}^{(1)})^2 \rho. \quad (3)$$

Here, the superscript on the shear velocity v_{it} represents the vibration direction of the shear wave.

The electrical impedance measurement was performed using an HP 4194 A impedance-gain-phase analyzer. The dielectric constant ϵ_{11}^S , ϵ_{22}^S , and ϵ_{33}^S were determined from the measured electrical impedance in a high frequency far above the resonance frequency (30 MHz in our case). The piezoelectric coefficients e_{15} , e_{24} can be determined from the measured elastic and dielectric constants according to the following relations:

$$e_{15} = \sqrt{(c_{55}^D - c_{55}^E) \epsilon_{11}^S}, \quad (4)$$

$$e_{24} = \sqrt{(c_{44}^D - c_{44}^E) \epsilon_{22}^S}. \quad (5)$$

Therefore, total 11 independent material constants (c_{11}^E , c_{22}^E , c_{44}^E , c_{55}^E , c_{66}^E , c_{33}^D , c_{44}^D , c_{55}^D , ϵ_{11}^S , ϵ_{22}^S , and ϵ_{33}^S) were directly determined from the above measurements and are listed in Table I together with the 2 derived piezoelectric coefficients. These determined material constants were used for the parameter identification calculations of the remaining 6 unknown material constants from the impedance spectrum fitting.

Among the remaining unknown material constants, if the value of c_{33}^E is given, the piezoelectric coefficient e_{33} can be obtained from the measured constants c_{33}^D and ϵ_{33}^S based on the constitutive equation

$$e_{33} = \sqrt{(c_{33}^D - c_{33}^E) \epsilon_{33}^S}. \quad (6)$$

TABLE I. The determined material constants of $[011]_c$ poled PMN-0.28PT single crystal by direct measurements.

Elastic constants (10^{10} N/m ²)							
c_{11}^E	c_{22}^E	c_{44}^E	c_{55}^E	c_{66}^E	c_{33}^D	c_{44}^D	c_{55}^D
19.82	10.63	6.72	0.69	4.84	20.62	7.89	4.96
Dielectric constants			Piezoelectric constants (C/m ²)		Density (kg/m ³)		
$\epsilon_{11}^S(\epsilon_0)$	$\epsilon_{33}^S(\epsilon_0)$	$\epsilon_{33}^S(\epsilon_0)$	e_{15}	e_{24}	ρ		
651	923	780	15.68	9.75	8075		

Therefore, only six constants need to be identified among all 17 independent constants and we defined them to be the components of a vector $\mathbf{m} = (c_{12}^E, c_{13}^E, c_{23}^E, c_{33}^E, e_{31}, e_{32})$.

In general, the electrical impedance can be calculated by the electrical charge Q and electric potential $\phi(\omega)$ across the electrodes

$$Z(\omega) = \frac{\phi(\omega)}{j\omega Q}. \quad (7)$$

In our work, Eq. (7) was solved by the finite element method (FEM) using ANSYS software (ANSYS, Inc., Canonsburg, PA).

The determination of remaining unknown constants of [011]_c poled PMN-0.28PT single crystal from the measured impedance spectrum is a procedure involving the inverse of the forward problem. Based on the 11 measured constants, the initial guess of the unknown constants $\mathbf{m}_0 = (c_{12}^E, c_{13}^E, c_{23}^E, c_{33}^E, e_{31}, e_{32})$, the density and the dimensions of the sample, a forward calculation is performed to generate the simulated electrical impedance spectrum from 50 kHz to 900 kHz. Here, we have constructed a 6-dimensional vector $\mathbf{m}$ using the 6 unknown constants. Material constants are updated iteratively based on the minimization of the objective function using the classic Levenberg-Marquardt (LM) method. The objective function is defined as the sum of the squares of the differences between the simulated and measured resonance and anti-resonance frequencies

$$F(\mathbf{m}) = \sum_i w_i (f_i(\mathbf{m}) - f_i^{\text{exp}})^2, \quad (8)$$

where $f_i(\mathbf{m})$, f_i^{exp} are the simulated and measured resonant, anti-resonance frequencies of the i th mode, respectively; w_i is the weighting factor that reflects the confidence of the measured frequency and also the balance of the low and high frequencies.

In inverse calculations, sensitivity analysis need to be performed to find out the influence of each material constants on the vibration modes in the impedance spectrum. In our analysis, deviations of parameters c_{12}^E , c_{13}^E , c_{23}^E , c_{33}^E , e_{31} , and e_{32} were set to be 10%, 25%, 5%, 10%, 25%, and 25%, respectively. Effects of parameter variations are shown in Figure 2. It can be seen that the variation of c_{12}^E , c_{23}^E , and c_{33}^E have more significant influence on most of the resonance-antiresonance-pairs in the impedance spectrum than that of c_{13}^E . The variation of e_{32} has little influence on the first, second, fifth, sixth antiresonance frequencies and the sixth resonance frequency, while the variation of e_{31} has little influence on the first, second, sixth antiresonance frequencies and the sixth resonance frequency in the impedance spectrum.

To determine the remaining 6 independent constants of [011]_c poled PMN-0.28PT single crystal, a set of initial guess for $\mathbf{m}_0$ listed in Table II was used to start the iteration. According to the flow chart in Figure 3, the remaining 6 independent constants were determined from fitting the measured electrical impedance spectrum. Piezoelectric coefficient e_{33} can be calculated using Eq. (6). The identified results for the constants are shown in Table II and the simulated impedance curve obtained by FEM using the reconstructed material properties is compared with the measured one in

FIG. 2. Effects of the parameter variations of c_{12}^E , c_{13}^E , c_{23}^E , c_{33}^E , e_{31} , and e_{32} on the calculated impedance spectrum.

Figure 4. One can see that the simulated impedance curve using the reconstructed results agree well with the measured ones. Finally, a complete set of elastic, dielectric, and piezoelectric constants of [011]_c poled PMN-0.28PT single crystal was derived. Since only one small sample is used here, homogeneity of material and self-consistency for the full set constants are guaranteed. For comparison, material constants determined by the CUNR method using 7 samples were also

FIG. 3. Flow chart of determining $c_{12}^E, c_{13}^E, c_{23}^E, c_{33}^E, e_{31}, e_{32}$ of $[011]_c$ poled PMN-0.28PT single crystals.

TABLE II. Comparison of the initial values, reconstructed results obtained by the proposed method and that obtained by ultrasonic and resonant method using 7 samples. (Unit for elastic stiffness constants $c_{ij}^E, 10^{10} \text{ N/m}^2$).

	c_{12}^E	c_{13}^E	c_{23}^E	c_{33}^E	e_{31}	e_{32}	e_{33}
Initial guess values	7.58	1.48	8.25	15.53	1.81	-8.25	18.74
Values by this CUPNIS method	8.22	1.15	8.92	13.64	1.68	-7.16	21.95
Values by CUNR method using 7 samples ^a	8.30	1.12	8.97	13.82	1.45	-7.84	20.65

^aReference 14.

FIG. 4. Comparison between the measured and simulated impedance spectra.

listed in the table for comparison.¹⁴ The excellent agreement validated the CUPNIS method developed in this work.

To check the stability of the reconstructed results by the L-M method, simulations were performed with different initial guesses. First, a set of piezoelectric and elastic constants was selected as the original values. A simulated impedance curve, which was obtained by FEM using the original values and measured constants, was regarded as “the standard impedance curve.” Then, material constants were reconstructed using the L-M inverse scheme for different initial guesses by applying a random variation of $\pm 10\%$ to the original input values. The reconstructed results are compared to the original set and are shown in Table III. Good convergence was found for different initial guesses. Figure 5 illustrates the comparison of the impedance curves using the initial values (1#) and the reconstructed values using the original input values. Excellent agreement among all sets was found.

TABLE III. Influence of the initial guess (with $\pm 10\%$ random fluctuation) on the values of reconstructed results. (Elastic stiffness constants: $c_{ij}^E \cdot 10^{10} \text{ N/m}^2$).

	c_{12}^E	c_{13}^E	c_{23}^E	c_{33}^E	e_{31}	e_{32}	e_{33}
Original value	8.15	2.58	9.14	14.13	2.30	-7.61	21.17
#1 Initial guess	7.33	2.90	8.31	14.93	2.53	-8.25	19.82
Reconstructed value	8.15	2.58	9.14	14.14	2.3	-7.63	21.15
#2 Initial guess	8.63	2.40	9.64	13.72	2.21	-7.35	21.89
Reconstructed value	8.15	2.56	9.13	14.12	2.29	-7.60	21.18
#3 Initial guess	7.83	2.72	8.80	14.44	2.39	-7.83	20.65
Reconstructed value	8.14	2.59	9.14	14.14	2.31	-7.62	21.15
#4 Initial guess	8.97	2.32	10.05	13.45	2.19	-7.23	22.25
Reconstructed value	8.14	2.59	9.15	14.12	2.31	-7.62	21.18

FIG. 5. Comparison among the impedance spectra calculated using initial values (1#), reconstructed results, and true values.

In summary, we report here a strategy using the combined ultrasound pulse-echo and impedance spectroscopy for the determination of full set of material constants of piezoelectric single crystals having low $mm2$ symmetry using only one small sample of millimeter size. This CUPNIS method has been applied to determine the full set material constants of $[011]_c$ poled rhombohedral phase PMN-0.28PT single crystal. The feasibility and effectiveness of this proposed method have been verified by comparing the results with that determined by the combined ultrasonic and resonance method using 7 samples. The stability of this method was also confirmed by the fluctuation analysis of the initial guesses. Compared with previous measurement methods for $[011]_c$ poled single crystals, which require seven samples, our method only needs one small sample so that material homogeneity and data set self-consistency are guaranteed. This method could eliminate the sample to sample variation problem as well as substantially reduce the experimental workload. Since it can handle $mm2$ symmetry system, it can certainly be used for other systems with higher symmetries,

since the number of independent constants would be less than 17. For practical applications and theoretical studies, this method is very handy and useful for characterizing single crystals that are available only in small size. It also offers a way to counter the intrinsic limitation of the relaxor-Pt domain engineered systems for which the properties of the samples are strongly geometry and composition dependent. From our experience, the best sample size for this method is a few millimeters. Samples below millimeter size may not reflect the bulk properties considering the size effects.

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