Characterization of full set material constants of piezoelectric materials based on ultrasonic method and inverse impedance spectroscopy using only one sample

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The most difficult task in the characterization of complete set material properties for piezoelectric materials is self-consistency. Because there are many independent elastic, dielectric, and piezoelectric constants, several samples are needed to obtain the full set constants. Property variation from sample to sample often makes the obtained data set lack of self-consistency. Here, we present a method, based on pulse-echo ultrasound and inverse impedance spectroscopy, to precisely determine the full set physical properties of piezoelectric materials using only one small sample, which eliminated the sample to sample variation problem to guarantee self-consistency. The method has been applied to characterize the $[001]_C$ poled Mn modified $0.27\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $0.46\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.27PbTiO_3 single crystal and the validity of the measured data is confirmed by a previously established method. For the inverse calculations using impedance spectrum, the stability of reconstructed results is analyzed by fluctuation analysis of input data. In contrast to conventional regression methods, our method here takes the full advantage of both ultrasonic and inverse impedance spectroscopy methods to extract all constants from only one small sample. The method provides a powerful tool for assisting novel piezoelectric materials of small size and for generating needed input data sets for device designs using finite element simulations. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4821107>]

I. INTRODUCTION

Due to the excellent piezoelectric ($d_{33} > 1500$ pC/N) and electromechanical coupling properties ($k_{33} > 0.9$) of relaxor-based ferroelectric single crystals, such as $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PMN-PT) and $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ (PZN-PT), the performance of many electromechanical devices have been greatly enhanced, including transducers, sensors and actuators.^{1–12} In modern device design, finite element software packages are routinely used, which need to have the complete set of material properties of constituent materials as input. The accuracy of these material constants determines the accuracy of the design simulation. Unfortunately, material constants provided by the manufacturers often deviate from true values, the problem is particularly serious for piezoelectric materials.¹³ Experimental determination of these constants is laborious and requires the use of several specimens because there are many independent constants involved. In research on new piezoelectric materials, the new materials often do not have very large uniform size, particularly single crystal samples, hence, it is difficult to obtain the full set material coefficients.

Some characterization methods for piezoelectric materials have been developed using lesser number of samples in order to reduce the errors caused by sample to sample

variations.^{13–17} A combined ultrasonic and resonance technique can eliminate unreliable modes in the resonance method and the number of samples can be reduced to 3–7, depending on the symmetries.¹⁷ The method showed its advantages in the characterization of piezoelectric materials with very large piezoelectric coefficients and with electromechanical coupling factors close to 100%, for which some of the derived formulas become unstable.¹⁸ Nearly all full set material coefficients of relaxor-PbTiO₃ single crystals in the literature were characterized by the combined method. The disadvantage of the combined method is the requirement of relatively large sample size. The crystal being characterized must have large enough uniform volume, so that sufficient number of samples can be cut from it. A method based on the transmission of acoustic waves through immersed plate had been developed for the characterization of large PZT-5H samples.¹⁴ This method needs two samples with big dimensions and a water tank setup. A recent proposed using inverse impedance spectroscopy by finite-element method to identify material constants of piezoelectric transformers reduced the sample number to one.¹⁵ However, because only one mode was used to identify six material constants, it leads to large uncertainties. In general, the number of observed normal modes must be larger than the number of independent parameters to be identified in order to obtain reliable results. There was also an attempt to identify ten independent material constants of a piezoceramic disk by minimizing the

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difference between the electrical impedance spectrum calculated by the finite element method and that obtained experimentally.¹³ This method could reduce the number of sample to one, which totally eliminated the sample to sample variation problem. Unfortunately, several parameters, such as e_{15} , ϵ_{11}^S , are not sensitive to the electrical impedance spectrum, hence, the accuracy of the method will depend strongly on the initial guess in the iteration.¹⁶ Another inverse method using electrical impedance spectrum to determine the material parameters of a piezoceramic disc is to consider the spatially resolved surface normal velocities.¹⁶ But, measuring the spatially resolved surface normal velocities could not give materials constants directly and the method also needs expensive laser-scanning vibrometer. It is also inconvenient for parameter identification since the spatially resolved surface normal velocity cannot be obtained in each iteration step in the inverse algorithm. Both inverse methods mentioned above using electrical impedance spectra need a very large size uniform property sample, because there must be enough number of independent resonance modes to determine many unknown independent materials constants.

Ultrasonic pulse-echo method, described in the Institute of Electrical and Electronics Engineers (IEEE) standards on piezoelectricity, is often used to characterize the elastic constants of solid materials.²⁻⁸ It is worth mentioning that better accuracy could be obtained by ultrasonic method than the resonance method.^{6,14} But only a few independent constants can be measured from one sample by the pulse-echo ultrasonic method. In this paper, we reported a methodology by combining the ultrasonic and inverse impedance spectroscopy method to obtain all constants using only one sample, which guarantees self-consistency. Compared with previous reported methods for characterizing piezoceramic materials, our method is more accurate, more stable, and less dependent on the initial guess. It is especially advantageous for measuring samples without prior knowledge. Since ultrasonic method can reduce the number of unknowns, the computation time and the difficulty in parameters identification will be much reduced. More importantly, this method does not require bigger dimension samples, so that we could characterize crystals that could not be grown into bigger size with uniform quality.

The proposed method has been applied to characterize [001]_c poled Mn modified 0.27Pb(In_{1/2}Nb_{1/2})O₃-0.46Pb(Mg_{1/3}Nb_{2/3})O₃-0.27PbTiO₃ single crystal with high accuracy and self-consistency. In the procedure, the material constants, c_{11}^E , c_{44}^E , c_{66}^E , c_{33}^D , c_{44}^D , ϵ_{11}^S , ϵ_{33}^S , are measured using ultrasonic pulse-echo method and capacitance measurements. Then, only 4 constants are left to be identified by the Levenberg-Marquardt (LM) method based on the measured electric impedance spectrum. The validity of the presented method is confirmed by the combined ultrasonic and resonant method using additional number of samples. The stability of the presented method is also analyzed.

II. METHODOLOGY

For [001]_c poled Mn modified 0.27Pb(In_{1/2}Nb_{1/2})O₃-0.46Pb(Mg_{1/3}Nb_{2/3})O₃-0.27PbTiO₃ single crystal, the macroscopic symmetry is tetragonal 4mm, there are total 11

independent material constants, including: 6 elasticity coefficients (c_{11}^E , c_{12}^E , c_{13}^E , c_{33}^E , c_{44}^E , c_{66}^E), 3 piezoelectric coefficients (e_{31} , e_{33} , e_{15}), and 2 dielectric constants (ϵ_{11}^S , ϵ_{33}^S). In our work, the determination of full set material constants consists of three basic steps: (1) ultrasonic measurements to determine 5 independent elastic constants, (2) impedance measurement to determine 2 dielectric constants, (3) identification of remaining 4 material constants using the LM method to fit the measured impedance spectrum.

A. Measurement method

In order to obtain more accuracy constants and decrease the number of unknown parameters to be determined, the ultrasonic pulse-echo method was first used to measure the elastic constants. The specimen with a cube or rectangular parallelepiped shape is used for the ultrasonic measurement. The [001]_c poled single crystal specimen with 4mm symmetry is illustrated in Figure 1. The poling direction [001]_c is defined as axis 3, and the [100]_c and [010]_c directions defined as axes 1 and 2, respectively. All material constant notations used herein are referred to this coordinate system. Five elastic constants c_{11}^E , c_{44}^E , c_{66}^E , c_{33}^D , c_{44}^D can be determined from the phase velocities of ultrasonic waves propagating along different crystallographic directions of this sample according to the following formulas:

Along direction 1:

$$v_{1L} = \sqrt{\frac{c_{11}^E}{\rho}}, \quad v_{1T}^{(2)} = \sqrt{\frac{c_{66}^E}{\rho}}, \quad v_{1T}^{(3)} = \sqrt{\frac{c_{55}^D}{\rho}}. \quad (1)$$

Along direction 2:

$$v_{2L} = \sqrt{\frac{c_{22}^E}{\rho}}, \quad v_{2T}^{(1)} = \sqrt{\frac{c_{66}^E}{\rho}}, \quad v_{2T}^{(3)} = \sqrt{\frac{c_{44}^D}{\rho}}. \quad (2)$$

Along direction 3:

$$v_{3L} = \sqrt{\frac{c_{33}^D}{\rho}}, \quad v_{3T}^{(2)} = \sqrt{\frac{c_{55}^D}{\rho}}, \quad v_{3T}^{(3)} = \sqrt{\frac{c_{44}^E}{\rho}}, \quad (3)$$

where the superscript on the shear velocity v represents the particle displacement direction perpendicular to the wave propagation direction.

In a frequency range way above the resonance frequencies, the dielectric constant $\epsilon^S(\epsilon_{11}^S, \epsilon_{33}^S)$ may be calculated from the impedance $|Z|$,¹⁴

FIG. 1. The coordinate system of single crystal specimen with 4mm symmetry.

$$\varepsilon^S = \frac{d}{2\pi f|Z|\varepsilon_0 A}, \quad (4)$$

where d is the sample thickness; f is a frequency far above the resonance frequencies; $|Z|$ is the measured impedance magnitude; A is the sample electrode area; ε_0 is the permittivity of vacuum (8.85×10^{-12} F/m).

Considering,^{19,20}

$$e_{15} = \sqrt{(c_{44}^D - c_{44}^E)\varepsilon_{11}^S}, \quad (5)$$

we can directly determine 7 material constants from the ultrasonic and dielectric measurements: c_{11}^E , c_{44}^E , c_{66}^E , c_{33}^D , ε_{11}^S , ε_{33}^S , e_{15} .

B. Finite element modeling

The constitutive relationships for a piezoelectric material are^{19,20}

$$T = c^E S - e^T E, \quad (6)$$

$$D = eS + \varepsilon^S E, \quad (7)$$

where T and S denote mechanical stress and strain; E and D denote electric field and dielectric displacement; the material constant tensors, c^E , e , and ε^S stand for elastic, piezoelectric, and dielectric constants, respectively.

From Hamilton's principle, the equation of motion for piezoelectric materials is given by^{15,21}

$$M_{uu}\ddot{u} + C\dot{u} + K_{uu}u + K_{u\Phi}\Phi = F_{total}, \quad (8)$$

$$K_{u\Phi}^T u + K_{\Phi\Phi}\Phi = Q, \quad (9)$$

where M_{uu} and K_{uu} denote mass and mechanical stiffness matrices, respectively; C is the mechanical damping matrix; $K_{u\Phi}$ and $K_{\Phi\Phi}$ denote piezoelectric coupling and dielectric stiffness matrices; F_{total} and Q denote the mechanical body force and applied electrical charge, respectively.

The electrical impedance can be calculated using external electrical charge and potential on the electrode,

$$Z(\omega) = \frac{\phi(\omega)}{j\omega Q}, \quad (10)$$

where, ω , $\phi(\omega)$ stand for the angular frequency and the electric potential on the electrode, respectively.

In this work, finite element software ANSYS (ANSYS Inc., Canonsburg, PA) is used for the simulation. Given a set of material properties (eleven independent constants), the density and the dimensions of the sample, the electrical impedance can be simulated by harmonic analysis.

C. Parameter identification

The determination of unknown properties of a piezoelectric material is an inverse problem. Given a set of initial parameters, a forward calculation using finite element method is performed first to generate the electric impedance

spectrum. Then, the simulated resonance and anti-resonant frequencies are compared with the measured values. According to the relationships among different constants of piezoelectric materials, when the value of c_{33}^E is given, the piezoelectric coefficient e_{33} can be obtained based on the determined constants c_{33}^D and ε_{33}^S ,^{19,20}

$$e_{33} = \sqrt{(c_{33}^D - c_{33}^E)\varepsilon_{33}^S}. \quad (11)$$

Therefore, only four constants, c_{12}^E , c_{13}^E , c_{33}^E , and e_{31} , need to be identified from the impedance spectrum. Finally, the unknown parameters are defined to form a vector p , and determined through iteration,

$$p = (c_{12}^E, c_{13}^E, c_{33}^E, e_{31}). \quad (12)$$

During the iteration procedure, the material parameters are adjusted to minimize the objective function,

$$F(p_i) = w_i \sum_j (f_i(p_i) - f_i^{\text{exp}})^2, \quad (13)$$

where $f_i(p)$, f_i^{exp} are the corresponding calculated and measured resonant, anti-resonant frequencies of the i th mode, w_i is the weighting factor reflecting the confidence in the measured values. These weighting factors are between 0 and 1.

The LM method is a classical algorithm for nonlinear least-squares problems and is usually employed in parameter identification. It provides fast and straightforward convergence.^{16,22,23} In our work, after the initial parameter vector p was given, the parameter vector p_{i+1} for the subsequent iteration step is given by

$$p_{i+1} = p_i + \Delta p_i, \quad (14)$$

$$\Delta p_i = [J^T(p_i)J(p_i) + \lambda I]^{-1} J^T(p_i)(f_i(p_i) - f_i^{\text{exp}}), \quad (15)$$

where, t is the transpose of the matrix, the factor λ is decreased in subsequent iteration steps, I is the identity matrix, and $J(p_i)$ denotes the Jacobian matrix,

$$J(p_i) = \frac{\partial f(p_i)}{\partial p_i} = \frac{\Delta f(p_i)}{\Delta p_i}. \quad (16)$$

The output material parameter vector p_{i+1} is used in the next iteration. The algorithm will terminate until $\Delta p < \delta$ (where δ is a predefined small positive number). Finally, a set of materials constants can be determined. In the inverse algorithm, FEM is used to determine the simulated electric impedance of the sample, and the LM method is used as the optimizer for minimizing the objective function. The flow chart of the inverse scheme is shown in Figure 2.

III. RESULTS AND DISCUSSION

We applied this scheme to characterize [001]_c poled Mn modified 0.27Pb(In_{1/2}Nb_{1/2})O₃-0.46Pb(Mg_{1/3}Nb_{2/3})O₃-0.27PbTiO₃ (PIN-PMN-PT:Mn) single crystal using only one sample. The original crystal boule was grown using the modified Bridgman technique and the sample was oriented

FIG. 2. Flow chart of the inverse method.

using the Laue x-ray machine with an accuracy of 0.5° . The dimensions of the sample used for our measurement is $4.17 \text{ mm (L)} \times 3.26 \text{ mm (W)} \times 2.56 \text{ mm (T)}$ after polishing. Gold electrodes were sputtered onto the pair of $[001]_c$ surfaces and a 10 kV/cm field was used to pole the sample in silicone oil at room temperature. The density of the sample was measured by the Archimedes' principle.

Harmonic analysis was performed using finite element software ANSYS over a frequency range from 100 kHz to 1000 kHz under a sine voltage signal with the voltage peak of $V_p = 5 \text{ V}$. The frequency step is 1 kHz and the damping ratio is set to 0.002 .

A. Ultrasonic and dielectric measurements

A 15 MHz longitudinal wave transducer and a 20 MHz shear wave transducer were used for the ultrasonic measurements. The electric pulses used to excite transducers were generated by a Panametrics 200 MHz pulser/receiver (Model 5900PR), and the time-of-flight between echoes were measurement by a Tektronix 460A digital oscilloscope. The phase velocities and five calculated elastic constants are listed in Table I.

The electrical impedance and phase spectrum of the sample was measured by an HP 4194A impedance-gain-phase analyzer with a 16048A test fixture at room temperature. The clamped dielectric constant ϵ_{33}^S and ϵ_{11}^S were determined by the electrical impedance measurements in a high frequency range far above the resonance frequency. The piezoelectric

TABLE I. The measured results of elastic constants of PIN-PMN-PT: Mn single crystal poled along $[001]_c$.

	v_{1L}	$v_{1T}^{(2)}$	$v_{2T}^{(3)}$	v_{3L}	$v_{1T}^{(3)}$
Measured phase velocities (m/s)	3619	2733	3000	4293	2882
Elastic constants (10^{10} N/m^2)	c_{11}^E 10.8	c_{66}^E 6.16	c_{44}^D 7.42	c_{33}^D 15.2	c_{44}^E 6.85

coefficient e_{15} can be calculated using Eq. (5). The results are listed in Table II.

From the above measurements, 7 material constants: c_{11}^E , c_{44}^E , c_{66}^E , c_{33}^D , ϵ_{11}^S , ϵ_{33}^S , e_{15} were directly determined and used for finite element calculations.

B. Sensitivity analysis

To identify material constants using inverse iterations, sensitivity analysis is needed to determine the influence of each material parameter on calculated vibration modes in the electrical impedance curve. In the analysis, a set of initial parameter vector p was given first and shown as Table III. Based on the obtained material constants: c_{11}^E , c_{44}^E , c_{66}^E , c_{33}^D , ϵ_{11}^S , ϵ_{33}^S , e_{15} , the electric impedance spectrum was simulated by finite element method. In the sensitivity analysis, the deviations of parameters e_{31} , c_{12}^E , c_{13}^E , c_{33}^E were set to be 20% , 5% , 5% , and 5% , respectively. Effects of parameter variations for e_{31} , c_{12}^E , c_{13}^E , c_{33}^E are shown in Figures 3 and 4. One can see that the variations of e_{31} have little influence on the second and third antiresonance frequencies in the electrical impedance spectrum. On the other hand, the variation of c_{12}^E has significant influence on the resonance-antiresonance-pair except the second and third resonances, while parameter variations of c_{13}^E and c_{33}^E have significant influence on the second and third resonance-antiresonance-pair.

C. Parameters identification using inverse scheme

To determine remaining 4 independent material constants of $[001]_c$ PIN-PMN-PT: Mn single crystal, a set of parameter vector p was used as the initial guess as listed in Table III. Based on the measured material constants:

TABLE II. The results of dielectric constants and piezoelectric coefficient e_{15} of the sample.

	$\epsilon_{11}^S(\epsilon_0)$	$\epsilon_{33}^S(\epsilon_0)$	e_{15}
Values	1237	735	7.9

TABLE III. Comparison of the initial values, the results obtained by the proposed method, and that obtained by the resonant method with 5 samples. (Elastic stiffness constants: c_{ij}^E , 10^{10} N/m^2 .)

	c_{12}^E	c_{13}^E	c_{33}^E	e_{31}	e_{33}
Initial values	8.2	8.0	11.2	-5.4	16.13
Values by inverse method	9.11	8.81	10.22	-4.84	17.99
Values by resonant method with 5 samples	8.95	8.93	10.3	-5.03	17.8

FIG. 3. Effect of the parameter variations of e_{31} and c_{12}^E on the impedance spectrum.

c_{11}^E , c_{44}^E , c_{66}^E , c_{33}^D , ε_{11}^S , ε_{33}^S , e_{15} , the material properties were determined according to the flow chart in Figure 2. The results are shown in Table III. Figure 5 shows the comparison between the measured electrical impedance curve and the one obtained by FEM using the reconstructed material properties. Excellent agreement was found. As a validity check, we also list the material properties determined by the resonant method using 5 samples. Again, excellent agreement was found, which proved the validity of our method. Since only one sample is needed, the method is much simpler and the data set self-consistency is guaranteed.

D. Discussions

In order to test the stability of the inverse method, simulations were performed to investigate the influence of the initial guess and fluctuations of input measured data on the reconstructed material constants. A set of elastic and piezoelectric constants was given as the initial input values as listed in Table IV. From these input values and measured material constants, an electric impedance curve was simulated by the finite element method. Then, the LM inversion algorithm was applied to identify the material constants with

FIG. 4. Effect of the parameter variations of c_{13}^E and c_{33}^E .

FIG. 5. Measured and simulated electrical impedance spectrum.

a random variation of $\pm 5\%$ and $\pm 10\%$ to the initial guess. The reconstructed material constants are shown in Table IV. The relative error $\Delta\%$ is obtained for each data set by dividing the deviation of the reconstructed value over the original values. The results show that all constants can be reconstructed with high convergence for different given initial guesses. Figure 6 presents the comparison between the electrical impedance curve obtained by FEM using the initial values (4#), reconstructed material constants, and the original values. One can see that the electrical impedance curve obtained by the reconstructed material constants agree well with the one obtained using the original input values. Table IV also shows that the reconstructed results have smaller relative errors for the initial guesses with $\pm 5\%$ random variation than those with $\pm 10\%$ random variation.

Next, the influence of fluctuation in the input dielectric constants on the reconstructed material constants was investigated. In the simulation, the initial values (1#) in Table IV were used as the initial input values for c_{12}^E , c_{13}^E , c_{33}^E , e_{31} , random noises were added to the dielectric constants at relative high levels of $\pm 1\%$ and $\pm 5\%$, respectively. The reconstruct results were summarized in Table V. Since piezoelectric constants e_{33} and e_{15} are calculated based on dielectric constants, these two constants are also listed in the

TABLE IV. Effect of initial guess on the stability of reconstructed results. (Elastic stiffness constants: c_{ij}^E , 10^{10} N/m².)

		c_{12}^E	c_{13}^E	c_{33}^E	e_{31}	e_{33}
#1	Original values	8.41	8.39	9.68	-4.73	18.95
	Initial ($\pm 5\%$)	8.6	8.61	9.3	-4.6	19.59
	Reconstructed	8.41	8.36	9.64	-4.71	19.02
	$\Delta\%$	0	0.36	0.41	0.42	0.37
#2	Initial ($\pm 5\%$)	8.1	8.0	10.0	-4.85	18.39
	Reconstructed	8.4	8.34	9.59	-4.69	19.12
	$\Delta\%$	0.12	0.60	0.93	0.84	0.90
	Initial ($\pm 10\%$)	9.0	8.8	9.0	-4.4	20.08
#3	Reconstructed	8.44	8.3	9.55	-4.64	19.19
	$\Delta\%$	0.36	1.07	1.34	1.9	1.27
	Initial ($\pm 10\%$)	7.8	7.7	10.4	-5	17.67
	Reconstructed	8.39	8.33	9.56	-4.66	19.15
	$\Delta\%$	0.24	0.72	1.24	1.48	1.06

FIG. 6. Comparison between the electrical impedance curve obtained by FEM using the initial values (4#), reconstructed material constants and the original values.

TABLE V. Effect of fluctuation in dielectric constants on the stability of reconstruction results. (Elastic stiffness constants: c_{ij}^E , 10^{10} N/m².)

		c_{12}^E	c_{13}^E	c_{33}^E	e_{31}	e_{33}	e_{15}
Fluctuation	Original values	8.41	8.39	9.68	-4.73	18.95	7.9
	Reconstructed	8.42	8.36	9.65	-4.72	19.07	7.93
	$\Delta\%$	0.12	0.36	0.31	0.21	0.63	0.38
	Reconstructed	8.42	8.35	9.65	-4.71	19.34	8.07
$\pm 5\%$	$\Delta\%$	0.12	0.48	0.31	0.42	2.05	2.15

table. One can observe that the variations of dielectric constants have less influence on the reconstructed constants c_{12}^E , c_{13}^E , c_{33}^E , and e_{31} than those calculated constants e_{33} and e_{15} . In other words, the calculated material constants e_{33} and e_{15} are more sensitive to the uncertainty of dielectric constants than the reconstructed constants.

Generally speaking, the uncertainty of phase velocity is less than 1%.^{6,14} For comparison, the initial values (1#) in Table IV were also used as the initial values of c_{12}^E , c_{13}^E , c_{33}^E , and e_{31} , random noises were added to the phase velocities at $\pm 0.5\%$ and $\pm 1\%$, respectively. The reconstructed results are given in Table VI. Since piezoelectric constants e_{33} and e_{15} are calculated based on elastic constants, they are also listed in the same table. One can observe that the variations of elastic constants have significant influence on the reconstructed and calculated constants compared with dielectric constants. In other words, the reconstructed

TABLE VI. Effect of fluctuations in phase velocities on the stability of reconstruction results. (Elastic stiffness constants: c_{ij}^E , 10^{10} N/m².)

		c_{12}^E	c_{13}^E	c_{33}^E	e_{31}	e_{33}	e_{15}
Fluctuation	Original values	8.41	8.39	9.68	-4.73	18.95	7.9
	Reconstructed	8.39	8.35	9.66	-4.7	18.90	7.94
	$\Delta\%$	0.24	0.48	0.21	0.63	0.26	0.51
	Reconstructed	8.34	8.31	9.64	-4.77	18.75	7.98
$\pm 1\%$	$\Delta\%$	0.83	0.95	0.41	0.85	1.06	1.01

constants c_{12}^E , c_{13}^E , c_{33}^E , and e_{31} are more sensitive to the uncertainties of measured phase velocities than to the measured dielectric constants.

IV. SUMMARY AND CONCLUSION

In this paper, we report a methodology that can be used to precisely determine the full set of self-consistent physical properties of piezoelectric material using *only one small sample* by combining the ultrasonic pulse-echo method with inverse impedance spectroscopy method. The validity and effectiveness of this method is confirmed by comparison with established methods using multiple samples. The method has been applied to determine the complete set of material constants for [001]_c poled Mn modified 0.27Pb(In_{1/2}Nb_{1/2})O₃-0.46Pb(Mg_{1/3}Nb_{2/3})O₃-0.27PbTiO₃ single crystal using one sample with a rectangular parallelepiped shape. For the 11 independent material constants, 5 elastic constants can be determined by the ultrasonic method, 2 dielectric constants can be determined by high frequency electric impedance, while the remaining 4 constants c_{12}^E , c_{13}^E , c_{33}^E and e_{31} are identified using the LM iteration method based on the measured electric impedance spectrum. The stability of the presented method is verified by analyzing the variation of the initial guess values and the fluctuations of the measured input constants on the reconstructed material constants.

In contrast to our previously developed method using pulse-echo plus resonance technique, which needs several samples to guarantee data self-consistency through over determination, the current method only needs one sample so that self-consistency is automatically satisfied, since sample to sample variation is eliminated. We also showed that the method is rather stable, which is especially useful for measuring samples without prior knowledge. More importantly, this method only needs one small sample, which make it very handy for researchers trying to develop novel piezoelectric materials that often could not be made very large.

It is very exciting to develop a method, which can get all materials coefficients from one sample for the 4 mm symmetry system. It allowed us to determine the complete set of materials coefficients for the [001]_c poled Mn modified 0.27Pb(In_{1/2}Nb_{1/2})O₃-0.46Pb(Mg_{1/3}Nb_{2/3})O₃-0.27PbTiO₃ single crystal. For practical applications and theoretical studies, it is also very important to measure the complete set of material properties for [011]_c and [111]_c poled samples with high self-consistency. However, it is difficult to obtain a fully poled single domain single crystal by applying field along [111]_c due to the large switching strain. As for the [011]_c poled sample, there are 17 independent material coefficients, which could not be determined uniquely from the limited number of piezoelectric active modes showing in the impedance spectrum. In order to achieve the goal of determining all 17 independent coefficients from one sample, new techniques need to be developed in the future.

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