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Characterization of piezoelectric materials with large piezoelectric and electromechanical coupling coefficients

Wenhua Jiang *, Rui Zhang, Bei Jiang, Wenwu Cao

Materials Research Institute, The Pennsylvania State University, 164 Materials Research Laboratory, University Park, PA 16802-4800, USA

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Abstract

The relaxor based ferroelectric $(1-x)\mathrm{Pb}(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$x\mathrm{PbTiO}_3$ and $(1-x)\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$x\mathrm{PbTiO}_3$ single crystals provided new challenges in property characterization because their extraordinarily large piezoelectric coefficients and electromechanical coupling coefficients. Large errors may occur in some of the derived material constants using conventional characterization techniques. This paper will analyze the inadequacy of the traditional characterization methods and provide some basic guidelines for properly characterizing piezoelectric materials with extremely high piezoelectric and electromechanical coupling coefficients.

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1. Introduction

The relaxor based $(1-x)\mathrm{Pb}(\mathrm{Zn}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$x\mathrm{PbTiO}_3$ [PZN–PT] and $(1-x)\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$–$x\mathrm{PbTiO}_3$ [PMN–PT] domain engineered single crystal systems exhibit superior electromechanical property compared to PZT ceramics, which have been dominating piezoelectric applications for more than 40 years. Due to the extremely attractive application potential of these new single crystal piezoelectric materials in making ultrasonic transducers and piezoelectric actuators, extensive studies have been conducted on these crystals in recent years [1–6]. For both fundamental study and device design purposes, it is necessary to measure the complete set of elastic, piezoelectric and dielectric constants of these crystals. Although the methods presented in the IEEE standard for piezoelectric crystal characterization have been exclusively used in the past, such methods have encountered difficulties when applied to these PMN–PT and PZN–PT crystals. First, the extraordinary large piezoelectric coefficients d_{33} and d_{31} make some conversion formulae unstable [7,8]. Second, because several samples are needed to obtain all of the independent constants for these anisotropic materials, serious property fluctuations from sample to sample in these systems often make it impossible to obtain a self-consistent data set. Third, the properties of the multidomain single crystals strongly depend on their domain structures. Every sample needs to be poled after cutting, lapping and polishing, because these mechanical processes on poled samples may change their domain structures. Thus, every sample should have a pair of (0 0 1) faces available after cutting. This restricts the number of possible sample orientations. Hence, some elastic constants, such as the elastic constant c_{13}^{E}, cannot be determined directly by sound velocity measurements.

This paper is devoted to analyze the errors and problems encountered in the characterization of PZN–PT and PMN–PT single crystals using different methods. Based on this analysis, an optimum measurement strategy (OMS) for determination of a full set of material constants for these new piezoelectric crystals is formulated. The analysis and physical principles are valid in general for characterization of piezoelectric materials with very large piezoelectric and electromechanical coupling coefficients.

* Corresponding author.

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2. Measurement procedure

Following the same argument in previous studies [1–9], we treat the [0 0 1] poled PZN–PT and PMN–PT single crystals as pseudo-tetragonal with 4mm domain pattern symmetry. The fourfold axis is along the poling direction, i.e., [0 0 1] direction of parent cubic system. For the 4mm symmetry, there are total 11 independent material constants to be determined: 6 elastic, 3 piezoelectric and 2 dielectric constants. It is assumed that the free dielectric permittivities ε_{11}^{T} and ε_{33}^{T} are determined by capacitance measurements prior to the determinations of elastic and piezoelectric constants which are obtained by either ultrasonic or resonance method (RM).

2.1. Combined ultrasonic-resonant method

The details of combined ultrasonic-resonant method (CURM) are given in Refs. [7–10]. For characterization of 4mm piezoelectric crystals, five samples are usually employed: (1) a rectangular parallelepiped with dimensions along [1 0 0]/[0 1 0]/[0 0 1]; (2) a rectangular parallelepiped with dimensions along [1 1 0]/[$\bar{1}$ 1 0]/[0 0 1]; (3) a square plate with its major surface normal to the poling direction ([0 0 1]-plate); (4) a bar with its length along [0 0 1](k_{33}-bar); (5) a bar with its length along [1 0 0] and electroded surface normal to [0 0 1] (k_{31}-bar).

First, the sound velocities of longitudinal and shear waves along three pure mode directions [1 0 0], [0 0 1] and [1 1 0] of sample 1 and 2 are measured by using pulse-echo technique. Since shear waves could have their displacements parallel or perpendicular to the poling direction, we can measure totally eight independent velocities in the three pure mode directions. The relationships of these velocities with elastic stiffness constants are given in Table 1. Since there are two methods to determine c_{44}^{D}, its proper value may be the arithmetic average of the two measurements. There are four measurements to correlate three elastic constants c_{11}^{E}, c_{12}^{E} and c_{66}^{E}. The most probable values of these constants can be found by the least square fitting procedure.

In CURM, the resonance measurements are conducted for bar and plate resonators (sample 3–5). From the series (resonance) and parallel (anti-resonance) resonance frequencies of those resonators, we can determine k_{33}, k_{31} and k_t, s_{11}^{E}, s_{33}^{D} and c_{33}^{D} as well as d_{31}. The piezoelectric strain constant d_{33} can also be measured directly by using Berlincourt d_{33} meter.

Combining all the above-mentioned ultrasonic and resonance measurements the following material constants can be directly obtained: c_{11}^{E}, c_{12}^{E}, c_{44}^{E}, c_{66}^{E}, c_{33}^{D} and c_{44}^{D}; s_{11}^{E} and s_{33}^{D} as well as d_{31}. In addition, the electromechanical coupling coefficients k_t, k_{33} and k_{31} are also determined. Adding ε_{11}^{T} and ε_{33}^{T} obtained from capacitor measurements, there are totally 14 independent measurements.

2.2. Resonance method

The RM recommended by IEEE standard has been used to measure PZT ceramics with symmetry of ∞m, for which the number of independent material constants are the same as that of 6mm symmetry. The useful compositions of PMN–PT and PZN–PT systems have 3m rhombohedral symmetry, but the engineered domain structures have macroscopic symmetry of 4mm. Since radial mode does not exist for 4mm symmetry crystal, sample geometries different from those used in the measurements for 6mm crystals are prepared. Usually five samples are prepared. (1) [0 0 1]-plate; (2) Square plate with its major surface normal to [1 0 0] ([1 0 0]-plate); (3) k_{33}-bar; (4) k_{31}-bar; and (5) Bar with length rotated from [1 0 0] by 45° and electroded surface normal to [0 0 1] (45° k_{31}-bar). From the measurements of series (resonance) and parallel (anti-resonance) resonance frequencies of these resonators, the material constants that can be directly determined by RM are listed in Table 2.

3. Derived constants and error propagation

Although 14 and 11 material constants can be determined by CURM and RM, respectively, self-consis-

Table 1
Relationships between phase velocities and elastic constants for 4mm symmetry

v	$v_l^{[001]}$	$v_s^{[001]a}$	$v_l^{[100]}$	$v_{s\perp}^{[100]}$	$v_{s\parallel}^{[100]}$	$v_l^{[110]}$	$v_{s\perp}^{[110]}$	$v_{s\parallel}^{[110]}$
$\rho v^2 =$	c_{33}^{D}	c_{44}^{E}	c_{11}^{E}	c_{66}^{E}	c_{44}^{D}	$\frac{1}{2}(c_{11}^{E}+c_{12}^{E}+2c_{66}^{E})$	$\frac{1}{2}(c_{11}^{E}-c_{12}^{E})$	c_{44}^{D}

[a] In this case the shear wave is always with its displacement perpendicular to poling direction.

Table 2
Material constants determined by the RM

Resonator	[1 0 0]-plate	[1 0 0]-plate	k_{33}-bar	k_{31}-bar	45° k_{31}-bar
Mode	Thickness extensional	Thickness shear	Length extensional	Length extensional	Length extensional
Determined constants	k_t^2, c_{33}^{D}	k_{15}^2, c_{44}^{D}	k_{33}^2, s_{33}^{D}	k_{31}^2, s_{11}^{E}	$1/4[s_{66}^{E}+2(s_{11}^{E}+s_{12}^{E})]$

tency of these determined constants are not guaranteed. In order to check the self-consistency, we need to explicitly provide six independent elastic constants c_{ij}^{E} or s_{ij}^{D}, three independent piezoelectric constants e_{ij} or d_{ij}, two independent dielectric permittivities $\varepsilon_{ij}^{\mathrm{S}}$ or $\varepsilon_{ij}^{\mathrm{T}}$. For this purpose, some relevant constitutive relations and conversion formula are used. Since errors are unavoidable in all measurements, these errors will propagate to all the derived constants. Knowing how these errors influence the derived data is especially important for these new multi-domain crystals due to their large k_{33}, d_{33} and d_{31}. As shown below, the error propagation will make some of the derived quantities unstable.

If a quantity $q = f(x_1, x_2, \ldots)$ is related to some quantities $x_1, x_2, \ldots$ with errors $\delta x_1, \delta x_2, \ldots$, the error of q can be expressed as $\Delta q = \sum_i |\partial f/\partial x_i| \Delta x_i$ or $\Delta q = [\sum_i ((\partial f/\partial x_i)\Delta x_i)^2]^{1/2}$. Here we use the former expression, which will provide the upper limit for the total error. In the following calculations the signs of absolute value are ignored.

3.1. Combined ultrasonic-resonant method

From the measured constants there are several ways to derive the other unknown constants since we have an over-determination situation in CURM. Here we will discuss the derivation procedures by using a few examples. The data used here are the measured results for the 0.92PZN–0.08PT (PZN–8%PT) multi-domain single crystals. By examining the conversion formulae for 4mm symmetry crystals it is noticed that all measured quantities can be divided into three groups. First, the elastic constant c_{66}^{E} can be separated from others because it is not related to piezoelectric effect and there is a simple relation between elastic stiffness and compliance, i.e., $s_{66}^{\mathrm{E}} = 1/c_{66}^{\mathrm{E}}$. Second, c_{44}^{E}, c_{44}^{D} and $\varepsilon_{11}^{\mathrm{T}}$ can be grouped together because they are related only to e_{15}, d_{15}, $\varepsilon_{11}^{\mathrm{S}}$ and $s_{44}^{\mathrm{E}} = 1/c_{44}^{\mathrm{E}}$. Finally, c_{11}^{E}, c_{12}^{E}, c_{33}^{D}, s_{11}^{E} and s_{33}^{D}; $\varepsilon_{33}^{\mathrm{T}}$, k_{33}, k_{31}, k_t as well as d_{33} are interrelated. It is seen that the variation of a quantity in one group can affect only the quantity derived by using the quantities in the same group. For example, the variation of c_{66}^{E} can affect only the value of s_{66}^{E}. In other words, error propagation happens only within the same group. Our discussions will emphasize on the final group.

3.1.1. Procedure 1

In this procedure, all six independent elastic stiffness constants $c_{\alpha\beta}^{\mathrm{E}}$ are isolated first. In order to do so, c_{33}^{E} and c_{13}^{E} need to be derived. The quantity c_{33}^{E} can be easily obtained from the measured c_{33}^{D} and k_t by

$$c_{33}^{\mathrm{E}} = c_{33}^{\mathrm{D}}(1 - k_t^2). \tag{1}$$

The errors of the measurements of c_{33}^{D} and k_t will propagate to c_{33}^{E} by

$$\frac{\Delta c_{33}^{\mathrm{E}}}{c_{33}^{\mathrm{E}}} = \frac{\Delta c_{33}^{\mathrm{D}}}{c_{33}^{\mathrm{D}}} + 2\left(\frac{\Delta k_t}{k_t}\right)\left(\frac{k_t^2}{1 - k_t^2}\right). \tag{2}$$

If $k_t > 1/\sqrt{3}$, the term $(\Delta k_t/k_t)$ will be magnified. This is not a problem for PZN–8%PT because its k_t is only 0.45, so that $2k_t^2/(1 - k_t^2) = 0.5$, which will actually reduce the relative contribution of $\Delta k_t/k_t$ in Eq. (2). Thus, error of c_{33}^{E} will mainly come from the relative error of c_{33}^{D}. In order to determine c_{13}^{E} we can use the formula:

$$c_{13}^{\mathrm{E}} = -\frac{s_{13}^{\mathrm{E}}}{s_{33}^{\mathrm{E}}}(c_{11}^{\mathrm{E}} + c_{12}^{\mathrm{E}}). \tag{3}$$

This requires s_{13}^{E} and s_{33}^{E} to be determined first. The IEEE standard suggests to calculate s_{33}^{E} from the measured s_{33}^{D} and k_{33} by the following relation:

$$s_{33}^{\mathrm{E}} = s_{33}^{\mathrm{D}}/(1 - k_{33}^2). \tag{4}$$

In this case the relative error of s_{33}^{E} is given by

$$\frac{\Delta s_{33}^{\mathrm{E}}}{s_{33}^{\mathrm{E}}} = \frac{\Delta s_{33}^{\mathrm{D}}}{s_{33}^{\mathrm{D}}} + 2\left(\frac{\Delta k_{33}}{k_{33}}\right)\left(\frac{k_{33}^2}{1 - k_{33}^2}\right). \tag{5}$$

For PZN–8%PT the measured $k_{33} = 0.94$, then $2k_{33}^2/(1 - k_{33}^2) = 15.2$, which is to say that if there is a 1% error in k_{33}, the calculated s_{33}^{E} will have 15% error. This calculation method is obviously not very stable.

The other way to get s_{33}^{E} is from quasi-statically measured d_{33} using the formula

$$s_{33}^{\mathrm{E}} = \frac{d_{33}^2}{\varepsilon_{33}^{\mathrm{T}} k_{33}^2}. \tag{6}$$

In this case, relative error of calculated s_{33}^{E} is given by

$$\frac{\Delta s_{33}^{\mathrm{E}}}{s_{33}^{\mathrm{E}}} = 2\frac{\Delta d_{33}}{d_{33}} + \frac{\Delta \varepsilon_{33}^{\mathrm{T}}}{\varepsilon_{33}^{\mathrm{T}}} + 2\left(\frac{\Delta k_{33}}{k_{33}}\right) \tag{7}$$

which is dependent only on the relative error of k_{33} but not on its value. Thus, for piezoelectric materials with large k_{33} it is better to use Eq. (6) instead of Eq. (4) to determine s_{33}^{E}. After c_{33}^{E} and s_{33}^{E} have been determined s_{13}^{E} may be calculated by

$$s_{13}^{\mathrm{E}} = -\left(\frac{s_{33}^{\mathrm{E}}(s_{33}^{\mathrm{E}} c_{33}^{\mathrm{E}} - 1)}{2(c_{11}^{\mathrm{E}} + c_{12}^{\mathrm{E}})}\right)^{1/2}. \tag{8}$$

The relative error is given by

$$\frac{\Delta s_{13}^{\mathrm{E}}}{s_{13}^{\mathrm{E}}} = \frac{1}{2}\left[\left(\frac{\Delta s_{33}^{\mathrm{E}}}{s_{33}^{\mathrm{E}}}\right)\left(\frac{2c_{33}^{\mathrm{E}} s_{33}^{\mathrm{E}} - 1}{c_{33}^{\mathrm{E}} s_{33}^{\mathrm{E}} - 1}\right) + \left(\frac{\Delta c_{11}^{\mathrm{E}}}{c_{11}^{\mathrm{E}}}\right)\frac{1}{(1 + c_{12}^{\mathrm{E}}/c_{11}^{\mathrm{E}})} + \left(\frac{\Delta c_{12}^{\mathrm{E}}}{c_{12}^{\mathrm{E}}}\right)\frac{1}{(1 + c_{11}^{\mathrm{E}}/c_{12}^{\mathrm{E}})} + \left(\frac{\Delta c_{33}^{\mathrm{E}}}{c_{33}^{\mathrm{E}}}\right)\frac{s_{33}^{\mathrm{E}} c_{33}^{\mathrm{E}}}{s_{33}^{\mathrm{E}} c_{33}^{\mathrm{E}} - 1}\right]. \tag{9}$$

For PZN–8%PT, $c_{33}^{\mathrm{E}} s_{33}^{\mathrm{E}} \gg 1$, thus Eq. (9) can be approximately expressed as

$$\frac{\Delta s_{13}^{E}}{s_{13}^{E}} = \frac{1}{2}\left[\left(\frac{\Delta c_{33}^{E}}{c_{33}^{E}}\right) + 2\left(\frac{\Delta s_{33}^{E}}{s_{33}^{E}}\right) + 0.51\left(\frac{\Delta c_{11}^{E}}{c_{11}^{E}}\right) + 0.49\left(\frac{\Delta c_{12}^{E}}{c_{12}^{E}}\right)\right]. \tag{10}$$

Finally, c_{13}^{E} is calculated from Eq. (3), and the relative error is given by

$$\frac{\Delta c_{13}^{E}}{c_{13}^{E}} = \left(\frac{\Delta s_{13}^{E}}{s_{13}^{E}}\right) + \left(\frac{\Delta s_{33}^{E}}{s_{33}^{E}}\right) + 0.51\left(\frac{\Delta c_{11}^{E}}{c_{11}^{E}}\right) + 0.49\left(\frac{\Delta c_{12}^{E}}{c_{12}^{E}}\right). \tag{11}$$

Up to this point, all six independent elastic stiffness constants under constant electric field have been determined. Since the elastic compliance matrix is the inversion of elastic stiffness matrix, all six independent elastic compliance constants $s_{\alpha\beta}^{E}$ can be easily determined. The directly measured s_{11}^{E} and s_{33}^{E} from the bar resonators can be used as consistency checks. The elastic constants derived by using this procedure are listed in Table 3. The constants labeled with a star ($*$) are the directly measured ones. The bold constants are those used in deriving the unknown constants.

3.1.2. Procedure 2

In this procedure all six independent elastic compliance constants $s_{\alpha\beta}^{E}$ are isolated first. The quantities s_{11}^{E} and s_{33}^{D} have been directly measured, s_{33}^{E} is obtained by using Eq. (6), and s_{12}^{E} is calculated by

$$s_{12}^{E} = s_{11}^{E} - \frac{1}{c_{11}^{E} - c_{12}^{E}}. \tag{12}$$

The relative error is given by

$$\frac{\Delta s_{12}^{E}}{s_{12}^{E}} = \frac{1}{s_{11}^{E}(c_{11}^{E} - c_{12}^{E}) - 1}\left[\left(\frac{\Delta s_{11}^{E}}{s_{11}^{E}}\right) s_{11}^{E}(c_{11}^{E} - c_{12}^{E}) + \left(\frac{\Delta c_{11}^{E}}{c_{11}^{E}}\right)\frac{c_{11}^{E}}{c_{11}^{E} - c_{12}^{E}} + \left(\frac{\Delta c_{12}^{E}}{c_{12}^{E}}\right)\frac{c_{12}^{E}}{c_{11}^{E} - c_{12}^{E}}\right]. \tag{12a}$$

Since $c_{11}^{E} - c_{12}^{E} \ll c_{11}^{E}$, c_{12}^{E} for PMN–PT and PZN–PT, the errors $(\Delta c_{11}^{E}/c_{11}^{E})$ and $(\Delta c_{12}^{E}/c_{12}^{E})$ will be magnified significantly. For example, the measured $c_{11}^{E} = 11.5$, $c_{12}^{E} = 10.5$ (10^{10} N/m^2) and $s_{11}^{E} = 90$ (10^{-12} m^2/N) for PZN–8%PT crystal. Then, the magnification factors of errors $(\Delta s_{11}^{E}/s_{11}^{E})$, $(\Delta c_{11}^{E}/c_{11}^{E})$ and $(\Delta c_{12}^{E}/c_{12}^{E})$ will be 9, 115 and 105, respectively. Thus s_{12}^{E} determined by this way will have very large error.

The constant s_{13}^{E} is obtained using the following formula:

$$s_{13}^{E} = -\sqrt{s_{33}^{E}\left[s_{11}^{E} - \frac{c_{11}^{E}}{(c_{11}^{E})^2 - (c_{12}^{E})^2}\right]}. \tag{13}$$

The error propagation is governed by

$$\frac{\Delta s_{13}^{E}}{s_{13}^{E}} = \frac{1}{2}\left(\frac{\Delta s_{33}^{E}}{s_{33}^{E}}\right) + \frac{c_{11}^{E}}{C}\left\{\left(\frac{\Delta s_{11}^{E}}{s_{11}^{E}}\right)s_{11}^{E}\frac{[(c_{11}^{E})^2 - (c_{12}^{E})^2]^2}{c_{11}^{E}} + \left(\frac{\Delta c_{11}^{E}}{c_{11}^{E}}\right)[(c_{11}^{E})^2 + (c_{12}^{E})^2] + 2\left(\frac{\Delta c_{12}^{E}}{c_{12}^{E}}\right)(c_{12}^{E})^2\right\}, \tag{13a}$$

where $C = 2[(c_{11}^{E})^2 - (c_{12}^{E})^2]\{s_{11}^{E}[(c_{11}^{E})^2 - (c_{12}^{E})^2] - c_{11}^{E}\}$. For the measured PZN–8%PT single crystals, the magnification factors of errors $(\Delta s_{11}^{E}/s_{11}^{E})$, $(\Delta c_{11}^{E}/c_{11}^{E})$ and $(\Delta c_{12}^{E}/c_{12}^{E})$ will be 1.2, 8 and 7, respectively. The error amplification is not as serious as that of s_{12}^{E}. The elastic compliance s_{44}^{E} and s_{66}^{E} are simply the reciprocals of c_{44}^{E} and c_{66}^{E}, respectively. After the six independent constants, $s_{\alpha\beta}^{E}$, are obtained, the elastic stiffness matrix can be derived by inverting the elastic compliance matrix. The elastic constants derived by using this procedure are listed in Table 4. Again, the constants with a star ($*$) are the directly measured ones and the others are derived quantities. The bold constants are those used in deriving the unknown constants.

From the above error analysis it is seen that Eqs. (3) and (8) are more stable than Eqs. (12) and (13), therefore, Procedure1 is preferred. However, we need to go further to isolate all 3 independent piezoelectric stress constants using the derived elastic constants and measured piezoelectric strain constants to check the self-consistency of the obtained data.

Table 3
Measured and derived material constants by Procedure 1

c_{11}^{E*}	c_{12}^{E*}	c_{13}^{E}	c_{33}^{E}	c_{44}^{E*}	c_{66}^{E*}
11.5	**10.5**	10.88	11.48	**6.3**	**6.5**
s_{11}^{E}	s_{12}^{E}	s_{13}^{E}	s_{33}^{E}	s_{44}^{E}	s_{66}^{E}
86.4	−13.56	−69.1	139.6	15.9	15.4
e_{15}	e_{31}	e_{33}	ε_{33}^{S}	ε_{11}^{S}	c_{44}^{D*}
10.9	−4.82	16	872	2687	**6.8**
ε_{33}^{T*}	ε_{11}^{T*}	k_{33}^{*}	k_{31}^{*}	k_{t}^{*}	d_{33}
7700	**2900**	**0.94**	**0.6**	**0.45**	**2900**

Units: c_{ij}: 10^{10} N/m^2; s_{ij}: 10^{-12} m^2/N; e_{ij}: C/m^2; d_{ij}: 10^{-12} C/N.

Table 4
Measured and derived material constants by Procedure 2

c_{11}^{E*}	c_{12}^{E*}	c_{13}^{E}	c_{33}^{E}	c_{44}^{E*}	c_{66}^{E*}
11.5	**10.5**	11.44	12.6	**6.3**	**6.5**
s_{11}^{E}	s_{12}^{E}	s_{13}^{E}	s_{33}^{E}	s_{44}^{E}	s_{66}^{E}
90	−10	−72.6	139.6	15.9	15.4
e_{15}	e_{31}	e_{33}	ε_{33}^{S}	ε_{11}^{S}	c_{44}^{D*}
10.9	4.69	25.6	873	2687	**6.8**
ε_{33}^{T*}	ε_{11}^{T*}	k_{33}^{*}	k_{31}^{*}	d_{33}	
7700	**2900**	**0.94**	**0.6**	**2900**	

Units: c_{ij}: 10^{10} N/m^2; s_{ij}: 10^{-12} m^2/N; e_{ij}: C/m^2; d_{ij}: 10^{-12} C/N.

3.1.3. Derivation of piezoelectric stress constants

First of all, d_{31} coefficient is readily obtained from the measured quantities

$$d_{31} = -\sqrt{\varepsilon_{33}^{T} s_{11}^{E} k_{31}^{2}}. \tag{14}$$

The errors of measured s_{11}^{E}, ε_{33}^{T} and k_{31} will propagate to the calculated d_{31} with the total relative error given by

$$\frac{\Delta d_{31}}{d_{31}} = \frac{1}{2}\left[\frac{\Delta\varepsilon_{33}^{T}}{\varepsilon_{33}^{T}} + \frac{\Delta s_{11}^{E}}{s_{11}^{E}} + 2\frac{\Delta k_{31}}{k_{31}}\right]. \tag{15}$$

From the measured c_{44}^{E} and c_{44}^{D}, the electromechanical coupling coefficient k_{15} is determined by

$$k_{15}^{2} = \left(1 - \frac{c_{44}^{E}}{c_{44}^{D}}\right). \tag{16}$$

The possible error of k_{15} determined by using the above formula depends on the ratio of c_{44}^{E}/c_{44}^{D}, which is

$$\frac{\Delta k_{15}}{k_{15}} = \frac{1}{2}\left(\frac{\Delta c_{44}^{D}}{c_{44}^{D}} + \frac{\Delta c_{44}^{E}}{c_{44}^{E}}\right)\left(\frac{c_{44}^{E}}{c_{44}^{E} - c_{44}^{D}}\right). \tag{17}$$

If the ratio $(c_{44}^{E}/c_{44}^{D}) > 2/3$, the error term $((\Delta c_{44}^{D}/c_{44}^{D}) + (\Delta c_{44}^{E}/c_{44}^{E}))$ will be magnified. For PZN–8%PT $(c_{44}^{E}/(c_{44}^{D} - c_{44}^{E})) = 12.6$, therefore, the term $((\Delta c_{44}^{D}/c_{44}^{D}) + (\Delta c_{44}^{E}/c_{44}^{E}))$ will be magnified by a factor of 6.3.

Since

$$k_{15}^{2} = \frac{d_{15}^{2}}{\varepsilon_{11}^{T} s_{44}^{E}} = \frac{d_{15}^{2} c_{44}^{E}}{\varepsilon_{11}^{T}}, \tag{18}$$

d_{15} is given by

$$d_{15}^{2} = \varepsilon_{11}^{T} k_{15}^{2}/c_{44}^{E} = \varepsilon_{11}^{T}\left(\frac{1}{c_{44}^{E}} - \frac{1}{c_{44}^{D}}\right). \tag{19}$$

The error of derived d_{15} can be estimated by

$$\frac{\Delta d_{15}}{d_{15}} = \frac{1}{2}\left[\left(\frac{\Delta\varepsilon_{33}^{T}}{\varepsilon_{33}^{T}}\right) + \left(\frac{\Delta c_{44}^{D}}{c_{44}^{D}}\right)\frac{c_{44}^{E}}{c_{44}^{D} - c_{44}^{E}} + \left(\frac{\Delta c_{44}^{E}}{c_{44}^{E}}\right)\frac{c_{44}^{D}}{c_{44}^{D} - c_{44}^{E}}\right]. \tag{19a}$$

The error magnification factors for $(\Delta c_{44}^{D}/c_{44}^{D})$ and $(\Delta c_{44}^{E}/c_{44}^{E})$ are 13.6 and 12.6, respectively. Thus the d_{15} determined using Eq. (19) may have large error. Now, the three independent piezoelectric strain constants d_{33}, d_{31} and d_{15} have been calculated from the measurement results. In principle, the piezoelectric stress constant e_{ij} can be derived by the corresponding conversion formula. For example, one may use

$$e_{31} = d_{31}(c_{11}^{E} + c_{12}^{E}) + d_{33}c_{13}^{E}, \tag{20}$$

$$e_{33} = 2d_{31}c_{13}^{E} + d_{33}c_{33}^{E} \tag{21}$$

and

$$e_{15} = d_{15}c_{44}^{E}. \tag{22}$$

If these formulas are used, the relative error of e_{31} and e_{33} can be estimated as the following. From Eq. (20), the relative error is

$$\frac{\Delta e_{31}}{e_{31}} = \frac{\Delta d_{31}(c_{11}^{E} + c_{12}^{E}) + d_{31}\Delta(c_{11}^{E} + c_{12}^{E}) + c_{13}^{E}\Delta d_{33} + d_{33}\Delta c_{13}^{E}}{d_{31}(c_{11}^{E} + c_{12}^{E}) + d_{33}c_{13}^{E}}. \tag{23}$$

The error of e_{31} caused only by the error of c_{12}^{E} is given by

$$\frac{\Delta e_{31}}{e_{31}} = \frac{d_{31}\Delta c_{12}^{E}}{d_{31}(c_{11}^{E} + c_{12}^{E}) + d_{33}c_{13}^{E}} = \left(\frac{\Delta c_{12}^{E}}{c_{12}^{E}}\right)\left[\frac{d_{31}}{d_{31}(1 + c_{11}^{E}/c_{12}^{E}) + d_{33}c_{13}^{E}/c_{12}^{E}}\right]. \tag{24}$$

For PZN–8%PT, $d_{33} = 2900$ pC/N, $d_{31} = -1450$ pC/N, $c_{11}^{E} = 11.5$, $c_{12}^{E} = 10.5$, and $c_{13}^{E} = 10.9$ (10^{10} N/m^2). Substituting these values into Eq. (24) leads to a very large error amplification factor for e_{31}:

$$\frac{\Delta e_{31}}{e_{31}} = 52.5\left(\frac{\Delta c_{12}^{E}}{c_{12}^{E}}\right). \tag{25}$$

Similarly, the error of e_{31} caused by the error of c_{13}^{E} is

$$\frac{\Delta e_{31}}{e_{31}} = \frac{d_{33}\Delta c_{13}^{E}}{d_{31}(c_{11}^{E} + c_{12}^{E}) + d_{33}c_{13}^{E}} = \left(\frac{\Delta c_{13}^{E}}{c_{13}^{E}}\right)\left[\frac{d_{33}}{d_{31}(c_{11}^{E} + c_{12}^{E})/c_{13}^{E} + d_{33}}\right]. \tag{26}$$

Inserting the data of PZN–8%PT into Eq. (26) yields

$$\frac{\Delta e_{31}}{e_{31}} = 109\left(\frac{\Delta c_{13}^{E}}{c_{13}^{E}}\right), \tag{27}$$

so that a very small change in c_{12}^{E} and c_{13}^{E} will cause very large error in the derived value of e_{31}. Also, we have

$$\frac{\Delta e_{33}}{e_{33}} = \frac{2c_{13}^{E}\Delta d_{31} + 2d_{31}\Delta c_{13}^{E} + c_{33}^{E}\Delta d_{33} + d_{33}\Delta c_{33}^{E}}{2d_{31}c_{13}^{E} + d_{33}c_{33}^{E}}. \tag{28}$$

The influence of the error in c_{33}^{E} on the calculated e_{33} can be estimated by

$$\frac{\Delta e_{33}}{e_{33}} = \left(\frac{\Delta c_{33}^{E}}{c_{33}^{E}}\right)\frac{d_{33}}{2d_{31}c_{13}^{E}/c_{33}^{E} + d_{33}}. \tag{29}$$

For the PZN–8%PT,

$$\frac{\Delta e_{33}}{e_{33}} = 19.2\left(\frac{\Delta c_{33}^{E}}{c_{33}^{E}}\right). \tag{30}$$

Similarly, the error of e_{33} caused by the error of c_{13}^{E} is

$$\frac{\Delta e_{33}}{e_{33}} = \left(\frac{\Delta c_{13}^{E}}{c_{13}^{E}}\right)\frac{2d_{33}}{d_{33}c_{33}^{E}/c_{13}^{E} + 2d_{31}}. \tag{31}$$

For PZN–8%PT

$$\frac{\Delta e_{33}}{e_{33}} = 36.3\left(\frac{\Delta c_{13}^{E}}{c_{13}^{E}}\right). \tag{32}$$

Thus, the calculated values of e_{31} and e_{33} are very sensitive to the values of c_{12}^{E} and c_{13}^{E}, especially to c_{13}^{E}.

Table 5
Relative error amplification factors of derived piezoelectric coefficients e_{31} and e_{33} caused by the variations of some elastic constants

	PZN–8%PT $d_{31}=-1450$ $d_{33}=2900$	PMN–33%PT $d_{31}=-1334$ $d_{33}=2820$	PZN–4.5%PT $d_{31}=-970$ $d_{33}=2000$	$BaTiO_3$ $d_{31}=-34.5$ $d_{33}=85.6$
$(\Delta e_{31}/e_{31})/(\Delta c_{12}^E/c_{12}^E)$	52.5	37.6	21.5	2.3
$(\Delta e_{31}/e_{31})/(\Delta c_{13}^E/c_{13}^E)$	109	78.9	43.8	4.9
$(\Delta e_{33}/e_{33})/(\Delta c_{33}^E/c_{33}^E)$	19.2	15.6	14.9	3.9
$(\Delta e_{33}/e_{33})/(\Delta c_{13}^E/c_{13}^E)$	36.6	31	28.7	7.2

We have calculated relative error amplification factors of the derived e_{31} and e_{33} for PZN–4.5%PT, PMN–33%PT, PZN–8%PT, and $BaTiO_3$, respectively. The results are listed in Table 5. The d_{31} and d_{33} values are also included in the table. It is seen that the larger the amplitudes of d_{31} and d_{33} are, the larger the relative errors of e_{31} and e_{33} are. When Eqs. (20) and (21) are used for $BaTiO_3$, there seems to be no problem because the smaller piezoelectric coefficients do not introduce large error amplification. Some conversion formulas become unstable when they are used for PZN–PT and PMN–PT single crystals since both d_{31} and d_{33} are very large in these systems.

The above analysis tells us that sometimes the error of a derived constant depends not only on the relative errors of measured quantities, but also on the absolute amplitude of these measured quantities and the calculation formula used. In some formulae, the error magnification factor often has the form of $x/(1-x)$ or $x^2/(1-x^2)$. These factors will rapidly increase as x approaches 1. This fact provides a serious challenge to the accurate characterization of material properties for these new piezoelectric crystals because the coupling coefficient k_{33} is very close to 1 and the piezoelectric and dielectric coefficients are also very large.

3.2. Resonance method

The RM can measure elastic constants s_{11}^E, s_{33}^D, c_{33}^D and one combination of $s = 1/4[s_{66}^E + 2(s_{11}^E + s_{12}^E)]$. The coefficients s_{33}^E and c_{33}^E can be obtained by using Eqs. (1) and (6). In order to derive s_{13}^E and s_{12}^E the following calculation procedure is used [11]:

First, the clamped dielectric permittivity ε_{33}^S is determined through the capacitance measurement of [0 0 1]-plate at a frequency far above its first parallel resonance. Then, the piezoelectric stress constant e_{33} is calculated by

$$e_{33} = \sqrt{k_t^2 c_{33}^D \varepsilon_{33}^S}. \tag{33}$$

Usually, ε_{33}^S cannot be determined with high accuracy, its error will transfer to derived e_{33} by

$$\frac{\Delta e_{33}}{e_{33}} = \frac{1}{2}\frac{\Delta\varepsilon_{33}^S}{\varepsilon_{33}^S}. \tag{34}$$

The piezoelectric stress constant e_{31} is calculated by

$$e_{31} = \frac{(\varepsilon_{33}^T - \varepsilon_{33}^S - d_{33}e_{33})}{2d_{31}}. \tag{35}$$

The errors of e_{33} and ε_{33}^S will propagate to e_{31}. The relative error of e_{31} is

$$\frac{\Delta e_{31}}{e_{31}} = \left[\frac{\varepsilon_{33}^S}{(\varepsilon_{33}^T - \varepsilon_{33}^S - e_{33}d_{33})}\right]\frac{\Delta\varepsilon_{33}^S}{\varepsilon_{33}^S} + \left[\frac{e_{33}d_{33}}{(\varepsilon_{33}^T - \varepsilon_{33}^S - e_{33}d_{33})}\right]\frac{\Delta e_{33}}{e_{33}}. \tag{36}$$

After e_{33} and e_{31} are determined, the elastic compliance s_{13}^E is given by

$$s_{13}^E = \frac{d_{33} - e_{33}s_{33}^E}{2e_{31}}. \tag{37}$$

The errors of e_{33} and e_{31} will transfer to the calculated s_{13}^E through

$$\frac{\Delta s_{13}^E}{s_{13}^E} = \frac{\Delta e_{31}}{e_{31}} + \frac{e_{33}s_{33}^E}{d_{33} - e_{33}s_{33}^E}\left(\frac{\Delta e_{33}}{e_{33}}\right). \tag{38}$$

The elastic compliance s_{12}^E and s_{66}^E are determined by

$$s_{12}^E = -s_{11}^E + \frac{2(s_{13}^E)^2}{s_{33}^E - 1/c_{33}^E} \tag{39}$$

and

$$s_{66}^E = 4s - 2(s_{11}^E + s_{12}^E), \tag{40}$$

where s is associated with the series resonance frequency of 45° k_{31}-bar resonator as indicated in Table 2.

The relative errors of the derived constants are estimated by

$$\frac{\Delta s_{12}^E}{s_{12}^E} = \frac{1}{-s_{11}^E + \frac{2(s_{13}^E)^2}{s_{33}^E - 1/c_{33}^E}}\left[s_{11}^E\left(\frac{\Delta s_{11}^E}{s_{11}^E}\right) + \frac{4(s_{13}^E)^2}{s_{33}^E - 1/c_{33}^E}\left(\frac{\Delta s_{13}^E}{s_{13}^E}\right) + \frac{2(s_{13}^E)^2 s_{33}^E}{(s_{33}^E - 1/c_{33}^E)^2}\left(\frac{\Delta s_{33}^E}{s_{33}^E}\right) + \frac{2(s_{13}^E)^2}{(s_{33}^E - 1/c_{33}^E)^2 c_{33}^E}\left(\frac{\Delta c_{33}^E}{c_{33}^E}\right)\right] \tag{41}$$

and

$$\frac{\Delta s_{66}^{E}}{s_{66}^{E}} = \frac{1}{4s - 2(s_{11}^{E} + s_{12}^{E})}\left[4s\left(\frac{\Delta s}{s}\right) + 2s_{11}^{E}\left(\frac{\Delta s_{11}^{E}}{s_{11}^{E}}\right) + 2s_{12}^{E}\left(\frac{\Delta s_{12}^{E}}{s_{12}^{E}}\right)\right]. \quad (42)$$

For the PZN–8%PT single crystal, we have

$$\frac{\Delta e_{31}}{e_{31}} = 3.03\left(\frac{\Delta \varepsilon_{33}^{S}}{\varepsilon_{33}^{S}}\right) + 0.57\left(\frac{\Delta e_{33}}{e_{33}}\right), \quad (43)$$

$$\frac{\Delta s_{13}^{E}}{s_{13}^{E}} = \frac{\Delta e_{31}}{e_{31}} + 3.44\left(\frac{\Delta e_{33}}{e_{33}}\right), \quad (44)$$

$$\frac{\Delta s_{12}^{E}}{s_{12}^{E}} = 4.97\left(\frac{\Delta s_{11}^{E}}{s_{11}^{E}}\right) + 7.94\left(\frac{\Delta s_{13}^{E}}{s_{13}^{E}}\right) + 4.22\left(\frac{\Delta s_{33}^{E}}{s_{33}^{E}}\right) + 36.74\left(\frac{\Delta c_{33}^{E}}{c_{33}^{E}}\right) \quad (45)$$

and

$$\frac{\Delta s_{66}^{E}}{s_{66}^{E}} = 42.96\left(\frac{\Delta s}{s}\right) + 11.69\left(\frac{\Delta s_{11}^{E}}{s_{11}^{E}}\right) + 1.95\left(\frac{\Delta s_{12}^{E}}{s_{12}^{E}}\right). \quad (46)$$

Thus, if there is an error of 10% in the measurement of ε_{33}^{S}, e_{33} will have an error of 5%, but the error of e_{31} will be 30%, and the derived s_{12}^{E}, s_{13}^{E} and s_{66}^{E} may have even larger errors.

4. Optimum strategy for characterization of PMN–PT and PZN–PT multi-domain single crystals

Comparing CRUM and RM, it is seen that the former yields more measurements from the same number of samples [7–10]. In RM, e_{33} is first determined through measuring k_t and ε_{33}^{S}, then the six independent elastic compliance constants can be isolated. However, to determine the clamped dielectric permittivity is not an easy job because the exactly clamped state of a sample is hard to realize. Such a measurement is avoided in the CRUM, but the derived e_{33} and e_{31} are very sensitive to variations of c_{13}^{E} and c_{12}^{E} when CRUM is applied to PMN–PT and PZN–PT systems, because k_{33} and d_{33} of these materials are very large. In comparison, the e_{33} and e_{31} derived from measured electromechanical coupling coefficients and clamped permittivities ε_{11}^{S} or ε_{33}^{S} will have smaller error because the errors of ε_{11}^{S} or ε_{33}^{S} will not be amplified when deriving e_{33} and e_{31}. After e_{33} or e_{31} is determined, a reversed strategy may be used, i.e., c_{13}^{E} is derived from measured e_{33} and e_{31}. For example, Eq. (21) yields that

$$c_{13}^{E} = \frac{e_{33} - d_{33}c_{33}^{E}}{2d_{31}}. \quad (47)$$

The error of measured e_{33} will transfer to c_{13}^{E} by

$$\frac{\Delta c_{13}^{E}}{c_{13}^{E}} = \left(\frac{1}{1 - d_{33}c_{33}^{E}/e_{31}}\right)\frac{\Delta e_{33}}{e_{33}}. \quad (48)$$

Since $d_{33}c_{33}^{E}/e_{31} \gg 1$ for measured PMN–PT or PZN–PT, the error of measured e_{33} will not be magnified, that is, c_{13}^{E} is not sensitive to the variation of e_{33}.

Another problem is the stability of conversion formulas from c_{ij} to s_{ij}. It is known that after c_{11}^{E}, c_{33}^{E}, c_{12}^{E} and c_{13}^{E} are determined, s_{11}^{E}, s_{33}^{E}, s_{12}^{E} and s_{13}^{E} can be calculated by

$$s_{11}^{E} = \frac{c_{11}^{E}c_{33}^{E} - c_{13}^{E2}}{c(c_{11}^{E} - c_{12}^{E})}, \quad (49a)$$

$$s_{12}^{E} = \frac{c_{13}^{E2} - c_{12}^{E}c_{33}^{E}}{c(c_{11}^{E} - c_{12}^{E})}, \quad (49b)$$

$$s_{33}^{E} = \frac{c_{33}^{E} + c_{12}^{E}}{c}, \quad (49c)$$

$$s_{13}^{E} = \frac{-c_{13}^{E}}{c} \quad (49d)$$

and

$$c = c_{33}^{E}(c_{11}^{E} + c_{12}^{E}) - 2c_{13}^{E2}. \quad (49e)$$

The error in determining c_{13}^{E} will transfer to the calculated s_{ij}. It is seen that

$$\frac{\Delta s_{11}^{E}}{s_{11}^{E}} = \frac{2c_{13}^{E2}c_{33}^{E}(c_{11}^{E} - c_{12}^{E})}{c(c_{11}^{E}c_{33}^{E} - c_{13}^{E2})}\left(\frac{\Delta c_{13}^{E}}{c_{13}^{E}}\right), \quad (50a)$$

$$\frac{\Delta s_{12}^{E}}{s_{12}^{E}} = \frac{2c_{13}^{E2}c_{33}^{E}(c_{11}^{E} - c_{12}^{E})}{c(c_{13}^{E2} - c_{12}^{E}c_{33}^{E})}\left(\frac{\Delta c_{13}^{E}}{c_{13}^{E}}\right), \quad (50b)$$

$$\frac{\Delta s_{33}^{E}}{s_{33}^{E}} = \frac{4c_{13}^{E2}}{c}\left(\frac{\Delta c_{13}^{E}}{c_{13}^{E}}\right) \quad (50c)$$

and

$$\frac{\Delta s_{13}^{E}}{s_{13}^{E}} = \frac{c_{33}^{E}(c_{11}^{E} + c_{12}^{E}) + 2c_{13}^{E2}}{c}\left(\frac{\Delta c_{13}^{E}}{c_{13}^{E}}\right). \quad (50d)$$

Since the value of c_{13}^{E} is very close to that of c_{11}^{E} and c_{33}^{E} for PMN–PT or PZN–PT crystals, i.e., $c_{33}^{E}(c_{11}^{E} + c_{12}^{E}) - 2c_{13}^{E2}$ and $c_{33}^{E}c_{11}^{E} - c_{13}^{E2}$ will be quite small, it is expected that the error of c_{13}^{E} will be magnified significantly. For the measured PMN–8%PT system, the error magnification factors for s_{11}^{E}, s_{33}^{E}, s_{12}^{E} and s_{13}^{E} are 13.2, 91.6, 30.9 and 31.9, respectively. In this case, the derived s-coefficients may have large errors. For the purpose of crosschecks, direct measurements of s_{11}^{E} and s_{33}^{E} are necessary.

With all of the above considerations, an OMS for determination of elastic and piezoelectric constants of PMN–PT and PZN–PT multi-domain single crystals may be as follows: (1) Use CURM to obtain 14 constants as described above. (2) e_{33} is determined through the measurements of electromechanical coupling coefficient k_t and clamped dielectric permittivity ε_{33}^{S}. (3) c_{13}^{E} is

Table 6
Material constants of PZN–8%PT multi-domain single crystal determined by OMS

c_{11}^{E}	c_{12}^{E}	c_{13}^{E}	c_{33}^{E}	c_{44}^{E}	c_{66}^{E}
11.5	10.5	10.9	11.51	6.3	6.5
s_{11}^{E}	s_{12}^{E}	s_{13}^{E}	s_{33}^{E}	s_{44}^{E}	s_{66}^{E}
87	−13.1	−70	141	15.8	15.4
e_{15}	e_{31}	e_{33}	d_{15}	d_{31}	d_{33}
10.1	−5.1	15.4	159	−1455	2890
$\varepsilon_{33}^{T^*}$	$\varepsilon_{11}^{T^*}$	ε_{33}^{S}	ε_{11}^{S}	k_{33}	k_{31}
7700	2900	984	2720	0.94	0.6

Units: c_{ij}: 10^{10} N/m^2; s_{ij}: 10^{-12} m^2/N; e_{ij}: C/m^2; d_{ij}: 10^{-12} C/N.

calculated by using Eq. (47). (4) After c_{11}^{E}, c_{33}^{E}, c_{12}^{E} and c_{13}^{E} are determined, s_{11}^{E}, s_{33}^{E}, s_{12}^{E} and s_{13}^{E} are calculated by using (50). (5) Compare the derived s_{11}^{E} and s_{33}^{E} with the measured s_{11}^{E} and s_{33}^{E} to check the consistency. If not meeting the requirements, go back and check each measurement. The most probable values may be obtained by the least squares fitting procedure for over determination situation. The material constants of PMN–8%PT obtained by using this OMS are shown in Table 6.

5. Fundamental principles for the elimination of unphysical data

The complete set of material constants shown in Table 6 is apparently self-consistent. But it is not guaranteed for the data to be physically reasonable because our OMS cannot eliminate the errors caused by property fluctuations from sample to sample. For the PMN–PT and PZN–PT multi-domain systems, we have used the following principles in discarding unreasonable data:

1. Energy conservation demands the electromechanical coupling coefficients to be always less than 1. Thus, large piezoelectric constants $d_{i\lambda}$ or $e_{i\lambda}$ demand large dielectric permittivity ε_{ij}. After a full set of constants has been determined, the electromechanical coupling coefficients for any vibration mode can be calculated. If any of these coupling coefficients is larger than 1, related data are in question.
2. When an elastic material deforms, the continuity requirement of matter must be satisfied. For example, Poison's principle requires that all three dimensions cannot expand (or contract) at the same time under uniaxial force or field. This demands some elastic compliance constants to be negative. It is known that s_{12}^{E} and s_{13}^{E} must be negative for 4mm symmetry crystals. Also the volume compressibility must be positive, i.e., $2s_{11}^{E}+2s_{12}^{E}+4s_{13}^{E}+s_{33}^{E}>0$ for 4mm symmetry crystals [12].
3. The elastic strain energy of a crystal should be positive. For 4mm symmetry crystals, this requires $c_{44}^{E}>0$, $c_{66}^{E}>0$, $c_{11}^{E}>|c_{12}^{E}|$, and $(c_{11}^{E}+c_{12}^{E})c_{33}^{E}>2(c_{13}^{E})^2$ [12]. Also, the condition $(s_{11}^{E}+s_{12}^{E})s_{33}^{E}>2(s_{13}^{E})^2$ needs to be satisfied.
4. From similar arguments as in 3, d_{31} must be negative for 4mm symmetry crystals. Since among the piezoelectric constants $(d_{ij}, e_{ij}, g_{ij}, h_{ij})$ all the constants should have the same signs, $d_{31}<0$ means that e_{31}, g_{31} and h_{31} should all be negative [13].

As an example, let us examine the two constant sets of PZN–8%PT domain engineered crystals obtained by the two calculation procedures presented in Section 3. The elastic constants given by the two procedures are both compatible with these principles. But, when this data is used to derive e_{31} using Eq. (20), it is found that the data set obtained using Procedure 2 leads to a positive $e_{31}(=4.69\ \mathrm{C/m^2})$. Thus, the data in Table 4 is not physical although it is self-consistent.

6. Summary and conclusions

Using conventional methods to determine the elastic and piezoelectric constants faces some difficulties in PZN–PT and PMN–PT single crystals with engineered domains. The coefficient s_{33}^{E} derived from Eq. (4) will be unstable because the value of k_{33} is near 1. Also the values of e_{31} and e_{33} derived from the conventional formulas Eqs. (20) and (21) become very sensitive to the values of c_{12}^{E} and c_{13}^{E} due to the large d_{31} and d_{33}. The derived values of s_{11}^{E}, s_{33}^{E}, s_{12}^{E} and s_{13}^{E} using the conversional formulas also become too sensitive to the variation of c_{13}^{E} because the value of c_{13}^{E} is very close to those of c_{11}^{E} and c_{33}^{E} for the measured PZN–PT single crystals. Since it is difficult to directly determine c_{13}^{E} with very high accuracy, a reversed strategy is suggested, i.e., to determine c_{13}^{E} through measured e_{33}. Based on the analysis given in this paper, an OMS for determination of elastic and piezoelectric constants of PMN–PT and PZN–PT multi-domain single crystals is proposed. In reality, this OMS may be system dependent. One should use detailed error analysis to determine the best strategy for each given material.

When a complete set of material constants is finally obtained by combining several measurements using different samples, the physical reasonability of the data set is not guaranteed because the OMS presented in this paper cannot eliminate the error caused by property fluctuation from sample to sample. One of the main reasons for the large property fluctuation from sample to sample in PMN–PT and PZN–PT crystal systems is the Pb lose during crystal growth and the extremely sensitive nature of the material properties to the chemical composition fluctuation. We found that 1% PT composition variation may cause 50% variation in some properties near the morphotropic phase boundary composition.

Thus, one should try to use samples with the same chemical composition (may be from different crystal boule) and the least number of samples if possible. Resonant ultrasonic spectroscopy technique [14] may be a possible way to resolve this problem since a complete set of material constants can be obtained by using only one sample. Finally, the guidelines presented in this paper are useful for checking the physical soundness of the data set to help eliminate unphysical data.

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