Temperature dependence of self-consistent full matrix material constants of lead zirconate titanate ceramics

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Up to date, there are no self-consistent data in the literature on the temperature dependence of full matrix material properties for piezoelectric materials because they are extremely difficult to determine. Using only one sample, we have measured the temperature dependence of full matrix constants of lead zirconate titanate (PZT-4) from room temperature to 120 °C by resonant ultrasound spectroscopy. Self-consistency is guaranteed here because all data at different temperatures come from one sample. Such temperature dependence data would make it a reality to accurately predict device performance at high temperatures using computer simulations. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4907412>]

Computer simulation has become an indispensable tool in modern industry. For accurate simulation designs and performance predictions, self-consistent material constants input is critical. In high power electromechanical devices, the temperature of the device will be increased due to heat generation. In order to simulate the actual device performance, we must know the temperature dependence of full matrix material constants. Unfortunately, it is not easy to perform such characterization, particularly when the material is strongly anisotropic, like piezoelectric materials.

There were some reported measurements of temperature dependence of full matrix data, but they were either for non-piezoelectric materials or for incomplete. Cao *et al.*^{1,2} measured the temperature dependence of the first and third order elastic constants of KMnF₃, which has a cubic symmetry and is non-piezoelectric so that there are only a few independent constants. Kamiya *et al.*³ investigated the temperature dependence of material parameters d_{31} , s_{11}^E , ϵ_{33}^T , and k_{31} of a tetragonal and a rhombohedral lead zirconate titanate (PZT) by the least squares fitting of complex admittance data, but the data set is incomplete and there is no way to check on their self-consistency. Sabat *et al.*⁴ investigated the temperature dependence of the full matrix material constants of soft and hard doped PZTs by the resonant method, in which five samples with different geometries were used. Zhang *et al.*⁵ studied the full matrix constants of Pb(Mg_{1/3}Nb_{2/3})O₃-PbZrO₃-PbTiO₃ piezocrystals at 30 °C, 50 °C, and 100 °C. In these reported measurements on piezoelectric materials, multiple samples with very different geometries must be used to determine the full matrix data at a given temperature.⁴⁻⁷ Sample to sample variation will lead to inconsistency of the full matrix material constants,^{8,9} and the problem becomes even worse at higher temperatures. For example, we have extracted the only set of available complete matrix data of PZT ceramics in the literature⁴ using the software Engauge.

Comparing the directly measured values of d_{15} and d_{33} with those calculated using the formula $d_{15} = k_{15} \sqrt{\epsilon_{11}^T s_{44}^E}$ and $d_{33} = k_{33} \sqrt{\epsilon_{33}^T s_{33}^E}$, we found that the data are not self-consistent even at room temperature and this inconsistency becomes worse with increasing temperature. At 165 °C, the inconsistency for d_{15} is more than 15%. If such inconsistent full matrix data were used for simulation designs, large errors would occur in the simulated results.

Why is such inconsistency unavoidable in the high temperature measurements of piezoelectric materials? The problem originates from the nature of ferroelectric materials. It is well known that the degree of poling in ferroelectric materials, such as PZT, depends on the sample geometry. It is hard to fully pole a long bar along the long axis but much easier to achieve full poling condition for a thin plate along the plate thickness direction. When temperature is increased, partial depoling will occur in ferroelectric materials, and the degree of depoling is also sample geometry dependent. Therefore, it is extremely difficult to obtain a self-consistent full matrix data at high temperatures using multiple different geometry samples. Ideally, if all constants could be measured from one sample, self-consistency would be guaranteed. Unfortunately, this is hard to do for piezoelectric materials because there are too many independent constants. It would require many independent measurements because the IEEE resonance method can only give two independent measurements for each geometry sample. Li *et al.*¹⁰ presented a method of using only one sample at room temperature, which is based on pulse-echo ultrasound and inverse impedance spectroscopy. They were able to precisely determine the full set physical properties of piezoelectric materials using only one small sample, but the method is hard to use at elevated temperatures. Therefore, up to date, there are no reports in the literature on the full matrix property characterization of piezoelectric materials at elevated temperatures using only one sample.

By using resonant ultrasound spectroscopy (RUS)¹¹⁻¹⁵ at high temperatures, we have achieved the accurate

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determination of the full matrix material constants of PZT-4 using only one sample. Our technique guarantees the matrix data self-consistent because all data measured at different temperatures come from the same sample; hence, errors caused by sample to sample variation in the IEEE method have been eliminated.

The poled PZT-4 ceramics has 10 independent material constants: 5 independent elastic stiffness constants at constant electric field, c_{11}^E , c_{12}^E , c_{13}^E , c_{33}^E , and c_{44}^E , 3 independent piezoelectric stress constants, e_{15} , e_{31} , and e_{33} , and 2 independent clamped dielectric constants, ϵ_{11}^S and ϵ_{33}^S . The temperature dependence of the full matrix material constants of PZT-4 ceramics was determined in two steps. First, the temperature dependence of clamped dielectric constants ϵ_{11}^S and ϵ_{33}^S was measured directly because they could not be determined by the RUS technique due to their poor sensitivity to mechanical resonance modes. The free dielectric constants ϵ_{11}^T and ϵ_{33}^T were measured at the same time and are used as consistency checks. The temperature dependence of elastic stiffness constants at constant electric field, c_{11}^E , c_{12}^E , c_{13}^E , c_{33}^E , and c_{44}^E , and the piezoelectric stress constants e_{15} , e_{31} , and e_{33} were determined by the RUS technique from the same sample.

For analyzing the vibration modes, we consider the sample geometry. A poled rectangular parallelepiped sample of PZT-4 has geometrical symmetry C_{2h} . There are four vibration groups of modes denoted by A_g , B_g , A_u , and B_u according to the deformation symmetry.¹⁴

Since the RUS technique does not require mode decoupling, the sample geometry can be any shape. A $4.461 \times 6.073 \times 4.914 \text{ mm}^3$ PZT-4 sample was fabricated. The density ρ determined from the volume and mass of the sample is 7609.2 kg/mm^3 . The high frequency and low frequency capacitances as functions of temperature were measured using an HP4294A impedance analyzer, connected to a temperature chamber (Delta 9023). Clamped and free dielectric constants were obtained from the high frequency capacitance at 35 MHz and the low frequency capacitance at 1 kHz, respectively. The measured ϵ_{11}^S and ϵ_{33}^S as a function of temperature can be fitted to the following polynomial functions:

$$\epsilon_{11}^S = 0.748 + 1.099 \times 10^{-3}T - 1.172 \times 10^{-6}T^2 + 6.637 \times 10^{-8}T^3 \quad (10^{-8} \text{ F/m}), \quad (1)$$

and

$$\epsilon_{33}^S = 0.632 + 1.384 \times 10^{-3}T - 5.350 \times 10^{-7}T^2 + 4.496 \times 10^{-8}T^3 \quad (10^{-8} \text{ F/m}). \quad (2)$$

Figure 1 is the RUS experimental setup. The sample, transmitting, and receiving transducers were fixed together and put into an air furnace (KSL 1100X). The dynamic resonance system (DRS Q9000) connected to a personal computer was used to generate the excitation signals and acquire the vibration resonance spectra. A thermometer (Fluke 51) was used to measure the temperature of the sample using a thermocouple. The spectra were measured from 20 °C to 120 °C at the temperature step $\Delta T = 5^\circ\text{C}$. The temperature

FIG. 1. RUS experimental setup.

control is approximately $\pm 0.3^\circ\text{C}$. To get sufficient modal frequencies, the resonance spectra were measured from 140 kHz to 640 kHz. It is inevitable that the resonance frequencies of some modes would be missing in the measured spectrum because they cannot be excited by the configuration. Thus, correctly identifying the modes is the most important step in the RUS measurement process.

The temperature dependence of the resonance frequency corresponding to each mode was fitted to a polynomial function. This fitting procedure serves two purposes. One is to reduce the random fluctuation of the measured data and the other is to obtain the resonance frequencies at temperatures in between the measured points. Based on our experience, there must be enough modes to ensure the accuracy of the inversion results. In general, the number of resonance frequencies measured should be at least 5 times, preferably 8–10 times, the number of parameters to be determined.¹³

The mode identification corresponding to each measured resonance frequency at the initial temperature serves as the reference for the next higher temperature mode identification. It would be impossible to correctly identify which measured frequency belongs to which mode at higher temperatures if the mode identification procedure at the initial temperature is wrong.

In our case, 53 modes between 140 kHz and 640 kHz were used in the inversion calculations at higher temperatures. The inversion procedure of material constants from resonance frequencies is the nonlinear least squares problem of finding a local minimizer of the deviation function

$$F = \sum_{i=1}^K w_i [f_{cal}^{(i)} - f_{meas}^{(i)}]^2, \quad (3)$$

where w_i is the weighting factor, and $f_{meas}^{(i)}$ and $f_{cal}^{(i)}$ are the i th resonance frequencies measured and calculated, respectively. A very elegant algorithm for this problem was proposed by Levenberg and Mauquardt.^{16,17} A library of FORTRAN subroutines based on LM algorithm, MINPACK,¹⁸ was used in our computation codes. To improve the inversion efficiency, the inversion results at the temperature T_1 were taken as the initial values at the next temperature point $T_1 + \Delta T$. During the inversion, $1/f_{meas}^{(i)2}$ was used as the weighting factor.

Figure 2 shows the inversion results of elastic stiffness constants c_{11}^E , c_{12}^E , c_{13}^E , c_{33}^E , and c_{44}^E , and Fig. 3 shows the

FIG. 2. Inversion results of elastic stiffness constants c_{11}^E , c_{12}^E , c_{13}^E , c_{33}^E , and c_{44}^E .

piezoelectric stress constants e_{15} , $-e_{31}$, and e_{33} . The inversion results at some temperatures are also given in Table I. In Fig. 2, the left and right y-axes correspond to $(c_{11}^E, c_{33}^E, c_{12}^E, c_{13}^E)$ and c_{44}^E , respectively. In Fig. 3, the left and right y-axes correspond to (e_{15}, e_{33}) and $-e_{31}$, respectively. The points in Figs. 2 and 3 are direct inversion results and the solid lines are fitted results. The fitted temperature dependence curves for these constants are

$$c_{11}^E = 13.765 + 7.824 \times 10^{-3}T - 1.778 \times 10^{-5}T^2 \quad (10^{10} \text{ N/m}^2), \quad (4)$$

$$c_{12}^E = 7.312 + 7.022 \times 10^{-2} \sqrt{T} - 3.480 \times 10^{-3}T \quad (10^{10} \text{ N/m}^2), \quad (5)$$

$$c_{13}^E = 7.470 + 8.690 \times 10^{-2}T - 4.470 \times 10^{-3}T \quad (10^{10} \text{ N/m}^2), \quad (6)$$

$$c_{33}^E = 12.479 + 8.667 \times 10^{-3}T - 2.223 \times 10^{-5}T^2 \quad (10^{10} \text{ N/m}^2), \quad (7)$$

$$c_{44}^E = 2.731 + 2.284 \times 10^{-3}T \quad (10^{10} \text{ N/m}^2), \quad (8)$$

$$e_{15} = 11.280 + 1.779 \times 10^{-3}T + 7.066 \times 10^{-5}T^2 \quad (\text{C/m}^2), \quad (9)$$

$$e_{31} = -(5.390 + 4.550 \times 10^{-3}T) \quad (\text{C/m}^2), \quad (10)$$

FIG. 3. Inversion results of piezoelectric stress constants e_{15} , $-e_{31}$, and e_{33} .

$$e_{33} = 14.935 + 7.990 \times 10^{-3}T + 8.636 \times 10^{-5}T^2 \quad (\text{C/m}^2). \quad (11)$$

Overall, the elastic stiffness constants c_{11}^E , c_{33}^E , and c_{44}^E and piezoelectric stress constants e_{15} , $-e_{31}$, and e_{33} increase with temperature from 20 °C to 120 °C. The constants c_{44}^E and $-e_{31}$ are nearly linear functions of temperature. In comparison, c_{12}^E and c_{13}^E are less sensitive to temperature variations as shown in Figure 2.

In order to verify the reliability of the inversion results, the free dielectric constants ϵ_{11}^T and ϵ_{33}^T are calculated from the inversion result using Eqs. (12)–(13), then compared with those directly measured,

$$\epsilon_{11}^T = \epsilon_{11}^S + e_{15}^2 s_{44}^E, \quad (12)$$

$$\epsilon_{33}^T = \epsilon_{33}^S + 2d_{31}e_{31} + d_{33}e_{33}, \quad (13)$$

where

$$d_{31} = e_{31}(s_{11}^E + s_{12}^E) + e_{33}s_{13}^E, \quad (14)$$

$$d_{33} = 2e_{31}s_{13}^E + e_{33}s_{33}^E. \quad (15)$$

The measured and calculated $\epsilon_{11}^T/\epsilon_0$ and $\epsilon_{33}^T/\epsilon_0$ are shown in Fig. 4. One can see that the relative errors $|(\epsilon_{11}^T(\text{cal}) - \epsilon_{11}^T(\text{meas}))/\epsilon_{11}^T(\text{meas})|$ and $|(\epsilon_{33}^T(\text{cal}) - \epsilon_{33}^T(\text{meas}))/\epsilon_{33}^T(\text{meas})|$ are below 1.6% and 2.4%, respectively, in the total temperature range of

TABLE I. Inversion results of c_{11}^E , c_{12}^E , c_{13}^E , c_{33}^E , c_{44}^E , e_{15} , e_{31} , and e_{33} , and the fitted values of ϵ_{11}^S and ϵ_{33}^S from measured results.

T (°C)	Inversion results								Fitted results	
	c_{11}^E (10^{10} N/m ²)	c_{12}^E	c_{13}^E	c_{33}^E	c_{44}^E	e_{15} (C/m ²)	e_{31}	e_{33}	$\epsilon_{11}^S/\epsilon_0$	$\epsilon_{33}^S/\epsilon_0$
20	13.910	7.544	7.761	12.644	2.784	11.328	-5.496	15.082	748	871
30	13.988	7.595	7.813	12.723	2.800	11.395	-5.522	15.254	762	881
40	14.051	7.627	7.848	12.789	2.817	11.473	-5.565	15.417	777	894
50	14.108	7.649	7.872	12.849	2.836	11.560	-5.610	15.581	795	910
60	14.171	7.661	7.883	12.908	2.860	11.652	-5.650	15.752	815	929
70	14.225	7.652	7.879	12.980	2.896	11.748	-5.714	15.906	838	950
80	14.276	7.654	7.883	13.033	2.920	11.866	-5.763	16.108	862	975
90	14.325	7.657	7.887	13.082	2.943	12.001	-5.809	16.328	889	1002
100	14.371	7.663	7.890	13.125	2.963	12.156	-5.848	16.577	917	1032
110	14.412	7.669	7.891	13.163	2.981	12.331	-5.887	16.858	948	1065
120	14.445	7.674	7.892	13.193	2.996	12.528	-5.925	17.181	982	1101

FIG. 4. Comparison between measured and predicted free dielectric constants. Solid line and up-triangles are for ϵ_{11}^T and Dashed line and down-triangles are for ϵ_{33}^T .

20°C–120°C. The differences between predicted and measured dielectric constants are well within the experimental errors. These control checks give us confidence on the obtained inversion results.

Figure 5 shows the temperature dependence of the resonance frequencies of A_u -3, B_u -2, A_g -13, and B_g -14 modes. The solid and dashed lines are calculated from the inversion results, while the points are directly measured results. One can see excellent agreement between the measured and calculated results.

In summary, we have extended the RUS technique to perform high temperature measurements and used it to investigate the temperature dependence of full matrix constants of PZT-4 ceramics. The parameters determined by this technique guarantee self-consistency because only one sample is

FIG. 5. Temperature dependence of resonance frequencies of vibration modes A_u -3, B_u -2, A_g -13, and B_g -14, where the solid and dashed lines are calculated using the inversion results and the points are measured results.

used, which eliminated errors from sample to sample variation. Undoubtedly, this procedure has unique advantages for studying the temperature dependence of full matrix property constants for piezoelectric materials. The key for this method is to properly excite and identify sufficient number of resonant modes. In general, the higher is the frequency, the more difficult it is to identify the mode due to the higher density of eigenfrequencies and their higher harmonics.

Our procedure and results paved the way for researchers to determine the temperature dependence of self-consistent full matrix properties of most piezoelectric materials. The method can also be applied to characterize other anisotropic non-piezoelectric solids at elevated temperatures so long as their Q-value is high enough. Such high temperature data can be used as input for finite element packages so that predictions on the high temperature performance of electromechanical devices through computer simulation become a reality.

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