

Video Article

Characterization of Full Set Material Constants and Their Temperature Dependence for Piezoelectric Materials Using Resonant Ultrasound Spectroscopy

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Abstract

During the operation of high power electromechanical devices, a temperature rise is unavoidable due to mechanical and electrical losses, causing the degradation of device performance. In order to evaluate such degradations using computer simulations, full matrix material properties at elevated temperatures are needed as inputs. It is extremely difficult to measure such data for ferroelectric materials due to their strong anisotropic nature and property variation among samples of different geometries. Because the degree of depolarization is boundary condition dependent, data obtained by the IEEE (Institute of Electrical and Electronics Engineers) impedance resonance technique, which requires several samples with drastically different geometries, usually lack self-consistency. The resonant ultrasound spectroscopy (RUS) technique allows the full set material constants to be measured using only one sample, which can eliminate errors caused by sample to sample variation. A detailed RUS procedure is demonstrated here using a lead zirconate titanate (PZT-4) piezoceramic sample. In the example, the complete set of material constants was measured from room temperature to 120 °C. Measured free dielectric constants ϵ_{11}^T and ϵ_{33}^T were compared with calculated ones based on the measured full set data, and piezoelectric constants d_{15} and d_{33} were also calculated using different formulas. Excellent agreement was found in the entire range of temperatures, which confirmed the self-consistency of the data set obtained by the RUS.

Video Link

The video component of this article can be found at <https://www.jove.com/video/53461/>

Introduction

Lead zirconate titanate (PZT) piezoelectric ceramics, $(1-x)\text{PbZrO}_3\text{-}x\text{PbTiO}_3$, and its derivatives have been widely used in ultrasonic transducers, sensors and actuators since the 1950s¹. Many of these electromechanical devices are used at high temperature ranges, such as for space vehicles and underground well logging. Moreover, high power devices, such as therapeutic ultrasonic transducers, piezoelectric transformers and sonar projectors, often heat-up during operation. Such temperature rises will change the resonance frequencies and the focal point of transducers, causing severe performance degradation. High intensity focused ultrasound (HIFU) technology, already used in clinical practice for the treatment of tumors, uses ultrasonic transducers made of PZT ceramics. During operation, the temperature of these transducers will increase, causing a change of the material constants of the PZT resonator, which in turn will change the HIFU focal point as well as the output power^{2,3}. The shift of focal point may lead to serious unwanted results, *i.e.*, healthy tissues being destroyed instead of cancer tissues. On the other hand, if the focal point shift can be predicted, one could use electronic designs to correct such shift. Therefore, measuring the temperature dependence of the full set material properties of piezoelectric materials is very important for the design and evaluation of many electromechanical devices, particularly high power devices.

Poled ferroelectric materials are the best piezoelectric materials known today. In fact, nearly all piezoelectric materials currently in use are ferroelectric materials, including solid solution PZT ceramics and $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$ (PMN-PT) single crystals. The IEEE (Institute of Electrical and Electronics Engineers) impedance resonance method requires 5-7 samples with drastically different geometries in order to characterize the full set material constants⁴. It is nearly impossible to obtain self-consistent full set matrix data using the IEEE impedance resonance method for ferroelectric materials because the degree of poling depends on the sample geometry (boundary conditions), while sample properties depend on the level of poling. To avoid problems caused by sample to sample variations, all constants should be measured from one sample. Li *et al.* reported the successful measurement of all constants from one sample at room temperature by using a combination of pulse-echo ultrasound and inverse impedance spectroscopy⁵. Unfortunately, this technique is hard to perform at elevated temperatures because it is not possible to perform ultrasonic measurements directly inside the furnace. There are also no commercially available shear transducers that can work at high temperatures. In addition, the coupling grease that bound the transducer and the sample cannot work at high temperatures.

In principle, the RUS technique has the capability to determine the full set material constants of piezoelectric materials and their temperature dependence using only one sample^{6,7}. But there are several critical steps for proper implementation of the RUS technique. First, the full set of tensor properties at room temperature should be accurately determined using a combination of pulse-echo and RUS techniques. Second, this room temperature data set can be used to predict the resonance frequencies and to match the measured ones in order to identify the corresponding modes. Third, for each small increment of temperature from room temperature up, one needs to perform spectrum reconstruction against the measured resonance spectrum in order to retrieve the full set constants at this new temperature from the measured resonance spectrum. Then, using the new data set as the new starting point, we can increase the temperature by another small temperature step to get the full set constants at the next temperature. Continuing this process will allow us to obtain the temperature dependence of the full set material constants.

Here, a PZT-4 piezoceramic sample is used to illustrate the measurement procedure of the RUS technique. The poled PZT-4 ceramic has ∞m symmetry with 10 independent material constants: 5 elastic constants, 3 piezoelectric constants and 2 dielectric constants. Because the dielectric constants are insensitive to the change of resonance frequencies, they were measured separately using the same sample. The temperature dependence of clamped dielectric constants ϵ_{11}^S and ϵ_{33}^S were measured directly from the capacitance measurements, while the free dielectric constants ϵ_{11}^T and ϵ_{33}^T measured at the same time were used as data consistency checks. The temperature dependence of elastic stiffness constants at a constant electric field c_{11}^E , c_{12}^E , c_{13}^E , c_{33}^E and c_{44}^E , and piezoelectric stress constants e_{15} , e_{31} and e_{33} were determined by the RUS technique using the same sample.

Protocol

1. Sample Preparation

Note: PZT-4 ceramic samples of the desired size can be directly ordered from many PZT ceramic manufacturers. One may also cut the sample from a larger PZT ceramic block using a diamond cutting machine, then repole the sample to restore depoling caused by cutting and polishing. Here, the sample shape is a parallelepiped with each dimension between 3 mm and 10 mm. Larger size samples are not necessary but accuracy might be compromised if samples are too small.

1. Polish the Surfaces of a Rectangular Parallelepiped Sample on a Plexiglas Disk Using Al_2O_3 Powders.
 1. First, glue the sample to the bottom surface of a metal rod using a very thin layer of wax by heating the rod and sample to 60 °C. Then cool down to room temperature. Tightly fit the rod into a metal cylinder with a larger outer diameter, so that the bottom surface of the cylinder and sample can be polished together to guarantee the flatness of the polished sample surface.
 2. Wet the glass plate using a water bottle then sprinkle 6 micron Al_2O_3 powders onto the wet surface. Place the sample holder with the sample glued to it onto the plate and make circular motion to grind the sample surface flat. Wash the Plexiglas plate and the sample holder thoroughly.
 3. Sprinkle 3 micron Al_2O_3 powders onto the wet glass plate and repeat the grinding again so that the sample surface will be smoother. Wash everything clean.
 4. Lift the sample off of the holder by heating the assembly to 60 °C to melt the wax. Clean the remaining wax on the sample surface using acetone.
 5. Polish all 6 surfaces of the sample using the same procedure.
2. Measure the dimensions of the sample using a μm and record the results. Here, the PZT-4 sample shown in **Figure 1** has the following dimensions: $l_x = 4.461$ mm, $l_y = 6.073$ mm, and $l_z = 4.914$ mm.
3. Measure the sample mass using a digital analytic balance.
4. Divide the mass by the volume to get the mass density ρ .

2. Pulse-echo Ultrasound Measurement

Note: In this paper, c_{ij}^E and c_{ij}^D represent the i^{th} row j^{th} column element of elastic stiffness tensors at constant electric field and constant electric displacement, respectively; s_{ij}^E and s_{ij}^D represent the i^{th} row j^{th} column element of elastic compliance tensors at constant electric field and constant electric displacement, respectively; d_{ij} represents the i^{th} row j^{th} column element of piezoelectric strain tensor; e_{ij} represents the i^{th} row j^{th} column element of piezoelectric stress tensor; ϵ_{ij}^S and ϵ_{ij}^T represent the i^{th} row j^{th} column element of clamped and free dielectric constants, respectively. All matrix material constants are in Voigt notation.

1. Turn on the Pulser-Receiver. Set the Mode to P/E for the pulse-echo measurement.
2. Connect a longitudinal wave transducer (15 MHz) and a digital oscilloscope to the Pulser-Receiver.
3. Put the transducer onto the sample surface along the x-direction with some coupling grease in-between. Note that the polarization direction is defined as the z-axis.
4. Press the CURSOR key on the control panel of the digital oscilloscope; press the side-menu button V Bars, then rotate the General Purpose knob to move one cursor line to the highest peak of the first echo signal.
5. Press the SELECT key, then rotate the General Purpose knob to move the other cursor line to the corresponding peak in the second echo signal.
6. Read the numerical value at the place marked with Δ : on the screen, which is the round trip time of flight, Δt_x^L , of the longitudinal wave pulse along the x-axis.
7. Calculate the longitudinal wave velocity along the x-direction, v_x^L , by dividing twice the thickness of the sample (round trip distance) by Δt_x^L , and then determine the elastic constant c_{11}^E using the formula: $c_{11}^E = \rho (v_x^L)^2$, where ρ is the sample density.

8. Repeat 2.3-2.5 using a shear wave transducer (5 MHz) and determine the shear wave velocity using the formula $v_x^{S1} = 2l_x / \Delta t_x^{S1}$, where Δt_x^{S1} is the time of flight for the shear wave round trip along the x-direction. Determine the shear elastic constant c_{66}^E using the formula $c_{66}^E = \rho (v_x^{S1})^2$.
9. Calculate the elastic constant c_{12}^E using the formula: $c_{12}^E = c_{11}^E - 2c_{66}^E$. This is the formula for the PZT sample with ∞m symmetry.
10. Place a shear transducer (5 MHz) onto the z-surface of the sample. Record the round trip time of flight, Δt_z^S , for the shear wave along the z-direction using the digital oscilloscope. Calculate the sound velocity v_z^S using the formula: $v_z^S = 2l_z / \Delta t_z^S$, and determine the elastic constant c_{44}^E using the formula: $c_{44}^E = \rho (v_z^S)^2$.

3. Measure the Temperature Dependence of Dielectric Constants

1. Apply a thin layer of conductive silver paint onto the two surfaces of the sample in the x-direction using a brush. The paint can be wiped off easily so that the same sample can be used for the RUS measurement later in open circuit condition.
2. Connect the impedance analyzer to the control computer and turn on both.
3. Set the start and stop frequencies of the impedance analyzer to 10 MHz and 40 MHz, respectively, for the frequency scan. Because the dielectric constant is $\gg 1$ for this PZT sample, calculate its dielectric constant ϵ_{11}^S using the parallel plate approximation $C^S = \frac{\epsilon_{11}^S A}{4\pi t}$, where the capacitance C^S is measured at 35 MHz, A is the electrode area and t is the thickness of the sample.
4. Connect the 16048A adapter to the four-terminal pair port of the impedance analyzer.
5. Press the CAL key of the impedance analyzer to display the calibration menu.
6. Press the ADAPTER key to display the Adapter Set in the starting Menu, and select 4TP 1M.
7. Connect the Lcur and Lpot terminals on the 16048A to the Hpot and Hcur terminals of 04294-61001. Other terminals remain in open circuit condition.
8. Press the SET OFUP key to display the Adapter Setup Menu.
9. Press the PHASE COMP [-] key to start the phase compensation data measurement. When the phase compensation data measurement is completed, the soft key label changes to PHASE COMP [DONE].
10. Connect the Lcur, Lpot, Hpot and Hcur terminals on the 16048A to the Lcur, Lpot, Hpot and Hcur terminals on the 04294-61001.
11. Press the LOAD [-] key to start the measurement. When the load data measurement is completed, the soft key label changes to LOAD [DONE].
12. Connect a fixture to the impedance analyzer, and keep it in an open circuit condition.
13. Press the CAL key, then press the soft key FIXTURE COMPEN to display the Fixture Compensation Menu.
14. Press the OPEN [-] key to start the open circuit data measurement. When the load data measurement is completed, the soft key label changes to OPEN [ON].
15. Short the fixture by placing a copper wire between the positive and negative leads.
16. Press the Short [-] key to start the short circuit data measurement. When the load data measurement is completed, the soft key label changes to Short [ON].
17. Fix a 100 Ω resistor to the fixture. Press the soft keys LOAD RESIST then DEFINE VALUE, enter 100 then press the key X1.
18. Press the LOAD key. When the load data measurement is completed, the soft key label changes to LOAD [ON]. Now calibration is completed.
19. Put the sample in the fixture then put the whole assembly into a temperature chamber and close the door.
20. Press the key MEAS on the impedance analyzer panel, and select $|c_p|$ -d.
21. Set the chamber temperature to 20 $^{\circ}\text{C}$ using the controlling computer.
22. Open the spreadsheet software installed in the computer connected to the impedance analyzer to read and record data from the impedance analyzer.
23. Read the capacitance data using a software in the computer and save the measured results into a file.
24. Change the chamber temperature with a temperature step of 5 $^{\circ}\text{C}$ by pressing the UP key on the control panel of the chamber. Repeat step 3.23 in each temperature increment after the chamber temperature becomes stable.
25. Determine the temperature dependence of the clamped dielectric constant ϵ_{11}^S based on the parallel capacitance formula using the capacitance value at 35 MHz, at which the capacitance becomes nearly frequency independent.
26. Reset the start and stop frequencies to 1 kHz and 10 kHz, respectively.
27. Repeat steps 3.21-3.24 to measure the temperature dependence of the low frequency capacitance of the sample. Save the measured result.
28. Determine the temperature dependence of the free dielectric constant ϵ_{11}^T using the low frequency capacitance at 1 kHz.
29. Remove the conductive silver paint on the sample surface using acetone.
30. Apply conductive silver paint to the two sample surfaces along the poling z-direction.
31. Repeat steps 3.3-3.28. Determine the temperature dependence of the clamped and free dielectric constants, ϵ_{33}^S and ϵ_{33}^T .

4. Resonance Frequencies Measurement at Room Temperature and Mode Identification

1. Measure the Resonance Frequencies.
 1. Put the sample in between the transmitting and receiving transducers of the RUS system with contacts only at the opposite corners of the sample (**Figure 2**). Note that the contacts are soft-spring loaded and the applied pressure is very light, just enough to hold the sample in place. Hence, no damages are caused by the contacts.
 2. Turn on the dynamic resonance system (**Figure 2**) and the computer connected to it.
 3. Run the control interface of the dynamic resonance system. Set the start frequency f_1 , the stop frequency f_2 , and the total number of data points N to be collected. Choose N so that $(f_1 - f_2)/N$ is less than 0.1 kHz to ensure frequency resolution. For this sample, set $f_1 = 200$ kHz, $f_2 = 450$ kHz and $N = 8,192$.
 4. Measure the resonance spectrum of the sample in this frequency range at room temperature and save the spectrum into a file.

5. Export ASCII data of the measured result to a file.
6. Open the ASCII data with a data plotting software. The first and second columns of the data matrix represent the real and imaginary parts of the response, respectively.
2. Identify Corresponding Modes for Measured Resonance Frequencies.
 1. Plot the frequency-amplitude curve (**Figure 3**). The peaks correspond to resonance frequencies of the sample.
 2. Calculate resonance frequencies using the measured room temperature full set tensor constants. The values of c_{11}^E , c_{12}^E , c_{44}^E were determined in steps 2.4-2.8. The values of ε_{11}^S and ε_{33}^S were determined in steps 3.25 and 3.31. Determine the shear piezoelectric constant e_{15} by the formula: $e_{15} = \sqrt{(\varepsilon_{11}^T - \varepsilon_{11}^S)c_{44}^E}$. Estimate the initial input values of c_{13}^E , c_{33}^E , e_{31} and e_{33} , based on materials constants measured using the combined technique from several samples. The equations for calculating the resonance frequency of to each mode are been given in Ref. 6.
 3. Compare the calculated resonance frequencies with those measured ones to identify corresponding modes for the measured resonance frequencies.
 4. Vary the guessed values of c_{13}^E , c_{33}^E , e_{31} and e_{33} iteratively to minimize the total global error between the calculated and measured resonant frequencies. The iteration stops when desired accuracy is reached.

5. Resonance Spectrum Measurement at Higher Temperatures and the Determination of Temperature Dependence of Full Set Material Constants

1. Measure Resonance Frequencies of the Sample at Higher Temperatures.
 1. Put the sample holder assembly into an air furnace (**Figure 4**). Use two high temperature coaxial cable wires through a hole on the furnace wall to connect the assembly to the RUS system.
 2. Put the sample in between the transmitting and receiving transducers that are already in the furnace, with contacts only at opposite corners of the sample.
 3. Put a thermocouple near the sample for actual temperature reading. Connect the thermocouple to a thermometer outside of the furnace.
 4. Close the furnace door.
 5. Turn on the control interface of the RUS system. Set the start and stop frequencies to 200 kHz and 450 kHz, respectively, and the number of data points to 8,192.
 6. Run the RUS system measuring software, measure the resonance frequencies of the sample and save the results into a file.
 7. Increase the temperature of the sample with a step of $\Delta T = 5^\circ\text{C}$. Repeat 5.1.6 until desired temperature is reached. Give each file saved a different name.

Note: The upper temperature limit is determined by the connection wires and transducers. Here, the RUS unit has an upper temperature limit of 200°C .
2. Determine the Temperature Dependence of the Full Set Material Constants.
 1. Repeat steps 4.1.5, 4.1.6 and 4.2.1 for every data set at different temperatures.
 2. Identify the mode of each resonance frequency. Use modes identified at temperature T as a reference for the next temperature $T + \Delta T$.
 3. Fit the temperature dependence of the measured resonance frequency corresponding to each mode into a simple function (for example, a linear or a quadratic function) using plotting software.
 4. Determine the full set material constants from the fitted resonance frequencies at each temperature using a self-written computer program that solves the RUS backward problem (**Figure 5**, **Figure 6**).

Note: Resonance frequencies of identified modes serve as input parameters to the numerical calculations. The procedure of determining material constants from resonance frequencies is a nonlinear least squares problem of finding a local minimizer of the deviation function $F = \sum_{i=1}^K w_i [f_{\text{cal}}^{(i)} - f_{\text{fit}}^{(i)}]^2$, where $f_{\text{cal}}^{(i)}$ is the calculated resonance frequency, $f_{\text{fit}}^{(i)}$ is the fitted resonance frequency from measured results, and w_i is the weighting factor. The computer code for the calculation of unknown material constants from measured resonance frequencies was written based on the Levenberg-Mauquardt (LM) algorithm⁸ and some FORTRAN subroutines in the MINPACK⁹ were called when implementing the LM algorithm.
3. Check the Self-consistency of the Full Set Material Constants.
 1. Calculate the free dielectric constants ε_{11}^T and ε_{33}^T from the inversion results and compare them with directly measured ones (**Figure 7**)¹⁰.
 2. Check the obtained data set to see whether they obey the condition of thermodynamic stability, for example, $(c_{11}^E + c_{12}^E)c_{33}^E > 2(c_{13}^E)^2$ for the PZT case.
 3. Compare the values of d_{15} calculated using $d_{15} = \sqrt{1 - c_{44}^E/c_{44}^D} \sqrt{\varepsilon_{11}^T s_{44}^E}$, and $d_{15} = e_{15}s_{44}^E$, and the values of d_{33} calculated using $d_{33} = 2e_{31}s_{13}^E + e_{33}s_{33}^E$ and $d_{33} = \sqrt{(s_{33}^E - s_{33}^D)\varepsilon_{33}^T}$.

Note: These relationships will differ for different symmetries, but the principle is the same. Generally, if the relative error is less than 5% between predicted and measured quantities, the results will be considered self-consistent¹¹. In some published data, even the sign would be wrong when a quantity is calculated using different formulas^{4,11}.

Representative Results

The LM algorithm used in the inversion is a local minimum finder. Therefore, the initial values of elastic stiffness constants c_{11}^E , c_{12}^E , c_{13}^E , c_{33}^E , and c_{44}^E , and piezoelectric constants, e_{15} , e_{31} and e_{33} should be given within a reasonable range from their true values. The constants c_{11}^E , c_{12}^E , and c_{44}^E , at room temperature can be precisely determined by the ultrasonic pulse-echo technique. The piezoelectric constants e_{15} at room temperature can be determined by the formula: $e_{15} = \sqrt{(\epsilon_{11}^T - \epsilon_{11}^S)} c_{44}^E$. Therefore, only values of c_{13}^E , c_{33}^E , e_{31} and e_{33} at room temperature need to be estimated in the beginning process. Traditional ultrasonic or resonant methods using several samples may be used to obtain the full set material constants at room temperature. Although results obtained by using several samples may be inconsistent, they are good enough to be used as the initial guess values of c_{13}^E , c_{33}^E , e_{31} and e_{33} .

Figures 5 and 6 show the measured elastic constant tensor components and piezoelectric coefficient tensor components, respectively, as a function of temperature for the demonstration sample PZT-4 ceramics¹⁰. One can see from **Figure 5** that the elastic constants c_{11}^E , c_{33}^E , and c_{44}^E increase with temperature while the elastic constants c_{12}^E and c_{13}^E are nearly independent of temperature in the temperature range from 20 to 120 °C. On the other hand, the piezoelectric constants e_{33} , e_{31} and e_{15} are strongly temperature dependent as shown in **Figure 6**.

Figure 7 is the comparison between measured dielectric constants (dots) under stress free condition and the predicted ones (lines) calculated based on the full set material constants obtained by the RUS method¹⁰. Excellent agreement was found for both ϵ_{11}^T and ϵ_{33}^T . In **Figure 8**, the dots represent piezoelectric constants d_{15} and d_{33} calculated using one set of formula while the lines represent their values calculated using another set of formula as given in step 5.3.3. Again, excellent agreement was found for both quantities. These results confirmed that the full set material constants obtained for the PZT-4 piezoceramic sample is highly self-consistent for the temperature range from 20 to 120 °C. The estimated relative errors of the constants measured by the RUS method are less than 3%. Note that if the full matrix material constants are not self-consistent, the integrity of the sample and mode identification process must be rechecked.

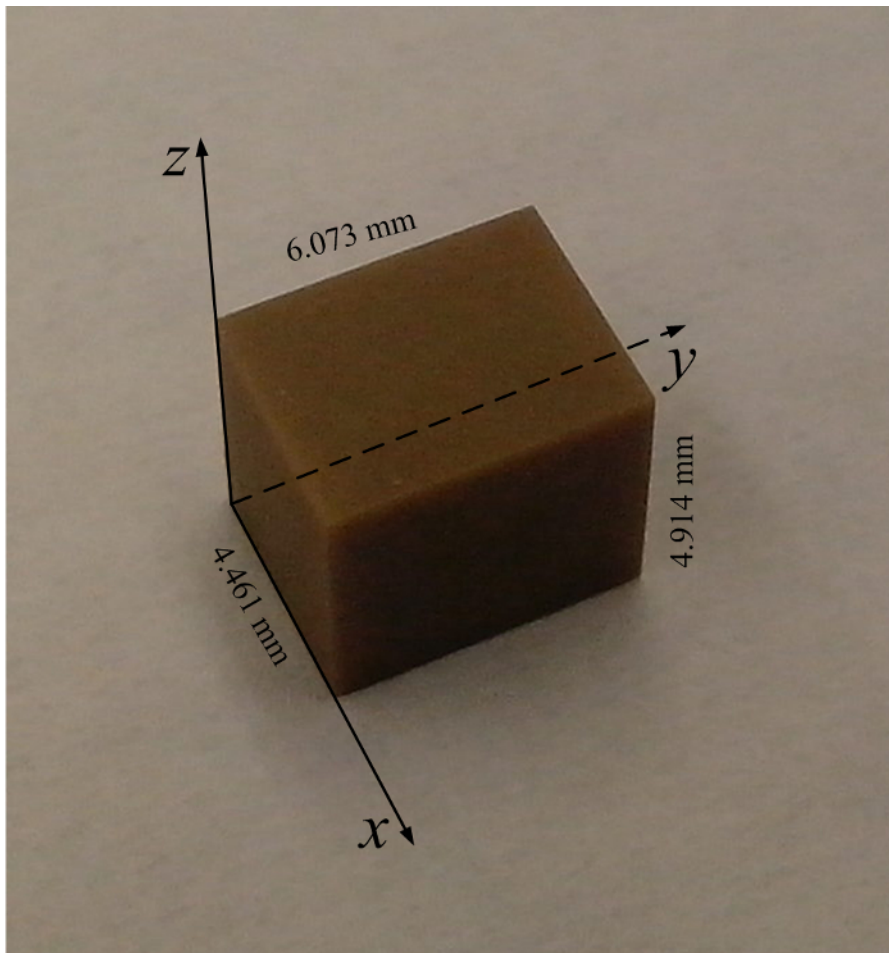


Figure 1: A rectangular parallelepiped PZT-4 piezoceramic sample. The dimensions measured by a micrometer are: $l_x = 4.461$ mm, $l_y = 6.073$ mm and $l_z = 4.914$ mm. The mass density of this sample is $7,609.2$ kg/mm³. [Please click here to view a larger version of this figure.](#)

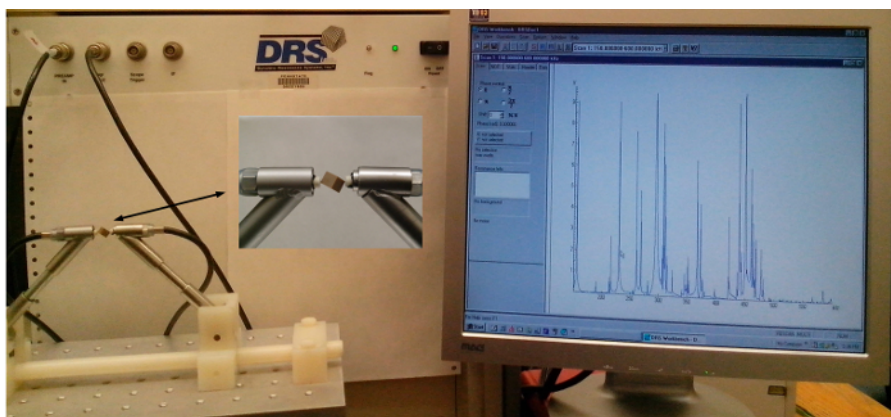


Figure 2: Experimental setup for measuring the resonance frequency spectrum. It consists of a dynamic resonant system and a computer. [Please click here to view a larger version of this figure.](#)

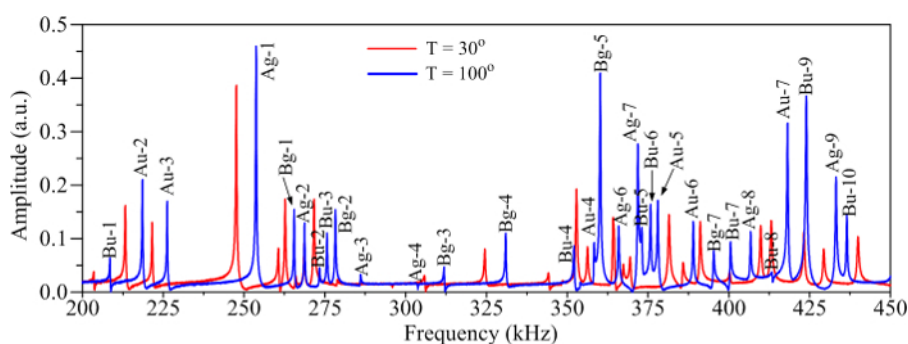


Figure 3: Resonant ultrasound spectrum of the sample shown in Figure 1 at 30 °C (red) and 100 °C (blue). The spectrum shifts slowly with the increase of temperature. Modes identified at room temperature can serve as the reference for higher temperature mode identification. The notation convention for resonance modes was given in reference⁶. [Please click here to view a larger version of this figure.](#)

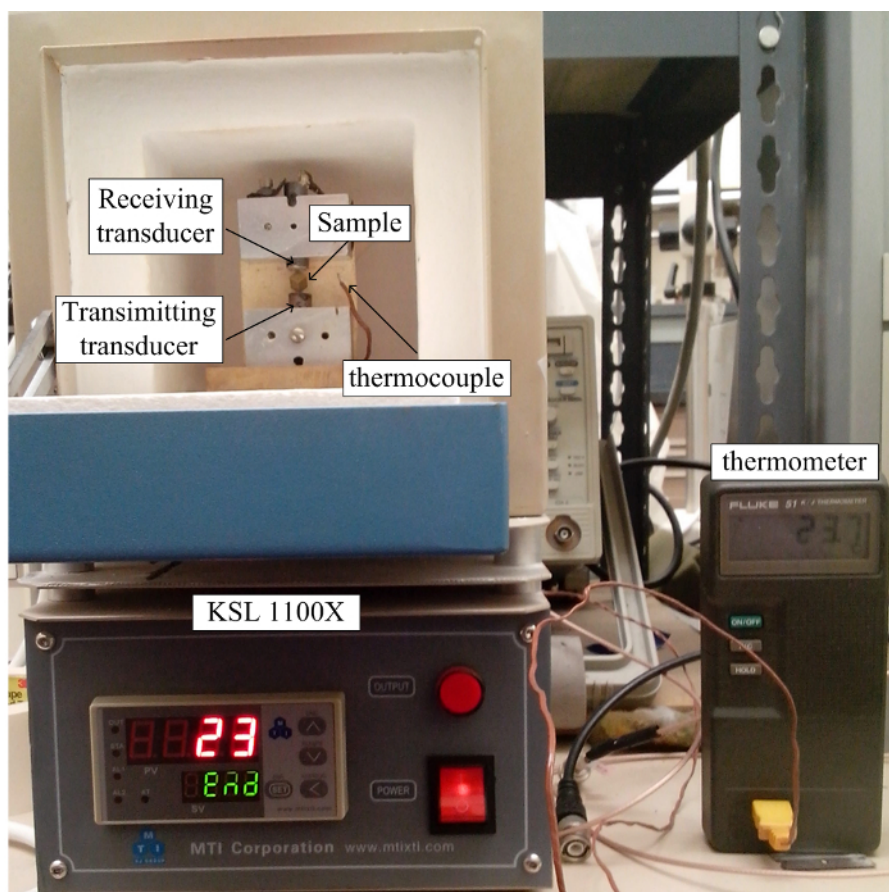


Figure 4: Air furnace with transmitting and receiving transducers inside. LiNbO_3 single crystals were used to make the transmitting and receiving transducers to endure high temperatures. A thermocouple was used to measure the temperature of the sample inside the furnace. [Please click here to view a larger version of this figure.](#)

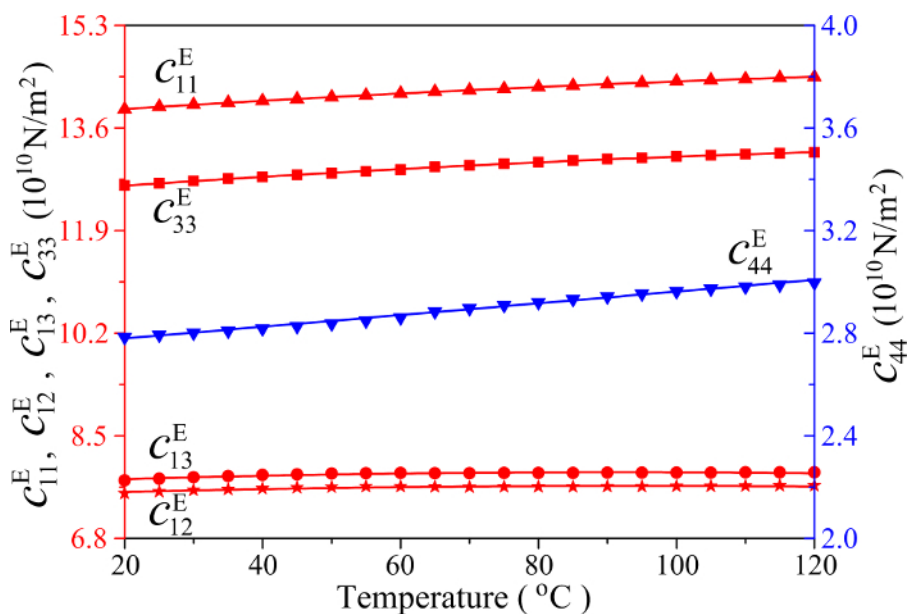


Figure 5: Inversion results of elastic stiffness constants c_{11}^E , c_{12}^E , c_{13}^E , c_{33}^E , and c_{44}^E . Overall, the elastic stiffness constants c_{11}^E , c_{33}^E and c_{44}^E increase with temperature from 20 to 120 $^{\circ}\text{C}$. Compared with c_{11}^E , c_{33}^E and c_{44}^E , the constants c_{12}^E and c_{13}^E are less sensitive to temperature. The constant c_{44}^E is nearly a linear function of temperature. This figure has been modified from reference¹⁰ with permission from AIP Publishing LLC. [Please click here to view a larger version of this figure.](#)

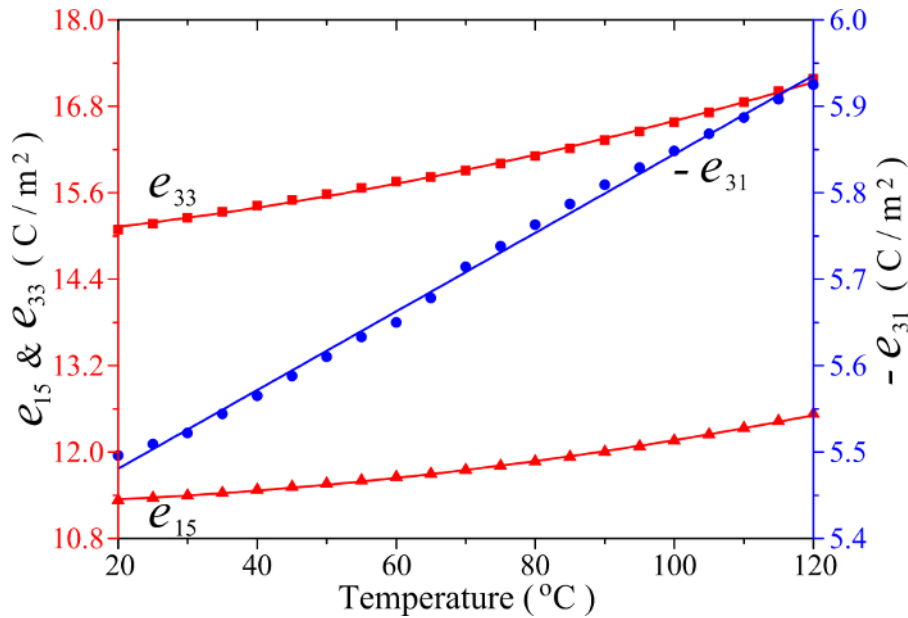


Figure 6: Inversion results of piezoelectric stress constants, e_{15} , $-e_{31}$ and e_{33} . The piezoelectric stress constants e_{15} , $-e_{31}$ and e_{33} increase with temperature from 20 to 120 °C. The constant $-e_{31}$ is nearly a linear function of temperature. This figure has been modified from reference¹⁰ with permission from AIP Publishing LLC. [Please click here to view a larger version of this figure.](#)

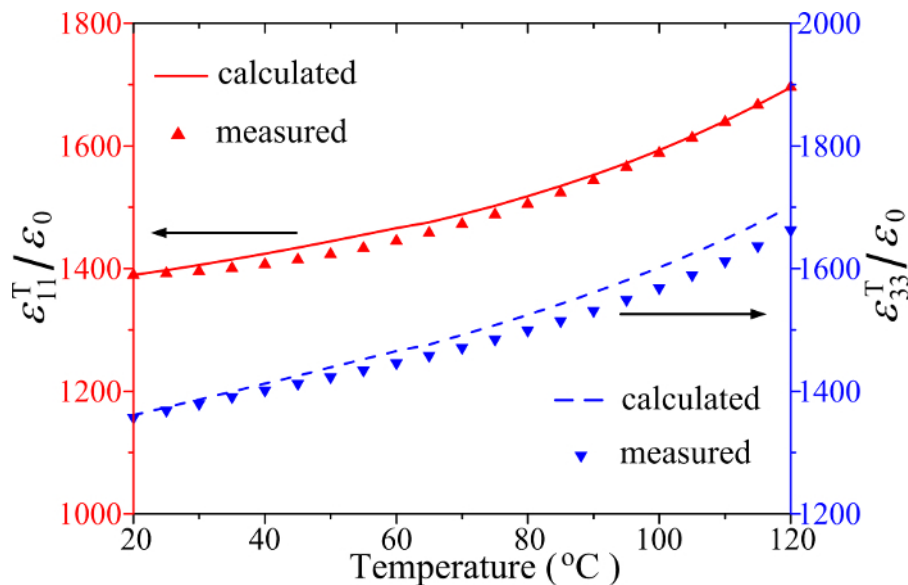


Figure 7: Comparison between measured and predicted free dielectric constants. Solid line and up-triangles are for ϵ_{11}^T ; dashed line and down-triangles are for ϵ_{33}^T . The relative errors $|(\epsilon_{11}^T(\text{cal}) - \epsilon_{11}^T(\text{meas})) / \epsilon_{11}^T(\text{meas})|$ and $|(\epsilon_{33}^T(\text{cal}) - \epsilon_{33}^T(\text{meas})) / \epsilon_{33}^T(\text{meas})|$ are below 1.6% and 2.4%, respectively, in the whole temperature range of 20-120 °C, where $\epsilon_{11}^T(\text{meas})$ and $\epsilon_{11}^T(\text{cal})$ are measured and calculated ϵ_{11}^T , respectively, and where $\epsilon_{33}^T(\text{meas})$ and $\epsilon_{33}^T(\text{cal})$ are measured and calculated ϵ_{33}^T , respectively. This figure has been modified from reference¹⁰ with permission from AIP Publishing LLC. [Please click here to view a larger version of this figure.](#)

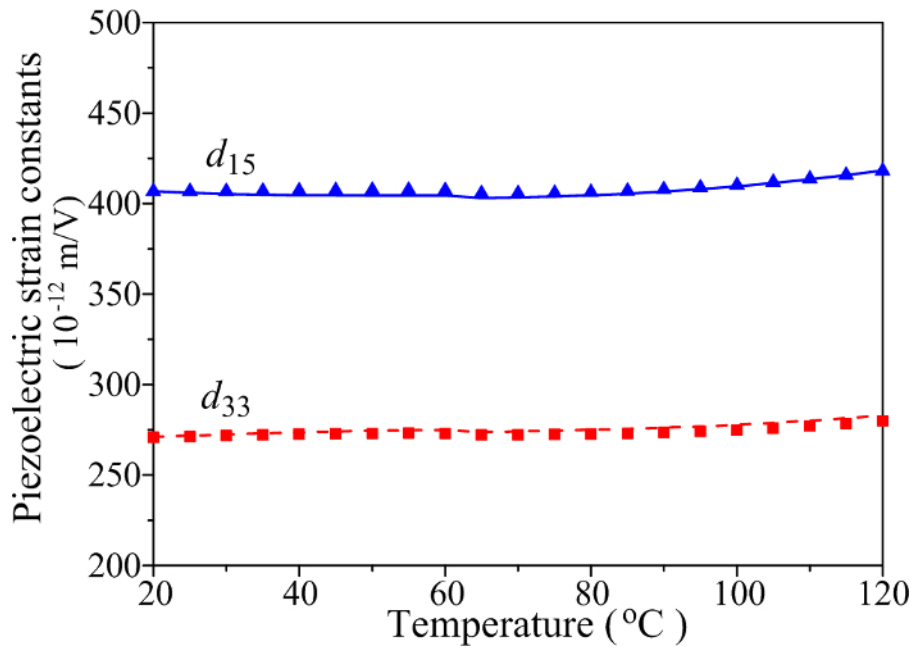


Figure 8: Comparison between d_{15} and d_{33} values calculated using different formulas. The calculation formulas for d_{15} are:

$d_{15} = \sqrt{1 - c_{44}^E / c_{44}^D} \sqrt{\varepsilon_{11}^T s_{44}^E}$ (blue solid line) and $d_{15} = e_{15} s_{44}^E$ (blue triangle), and for d_{33} are: $d_{33} = 2e_{31} s_{13}^E + e_{33} s_{33}^E$ (red dashed line) and

$d_{33} = \sqrt{(s_{33}^E - s_{33}^D) \varepsilon_{33}^T}$ (red square). The relative errors of d_{15} and d_{33} are below 0.8%, and 1.2%, respectively, in the whole temperature range.

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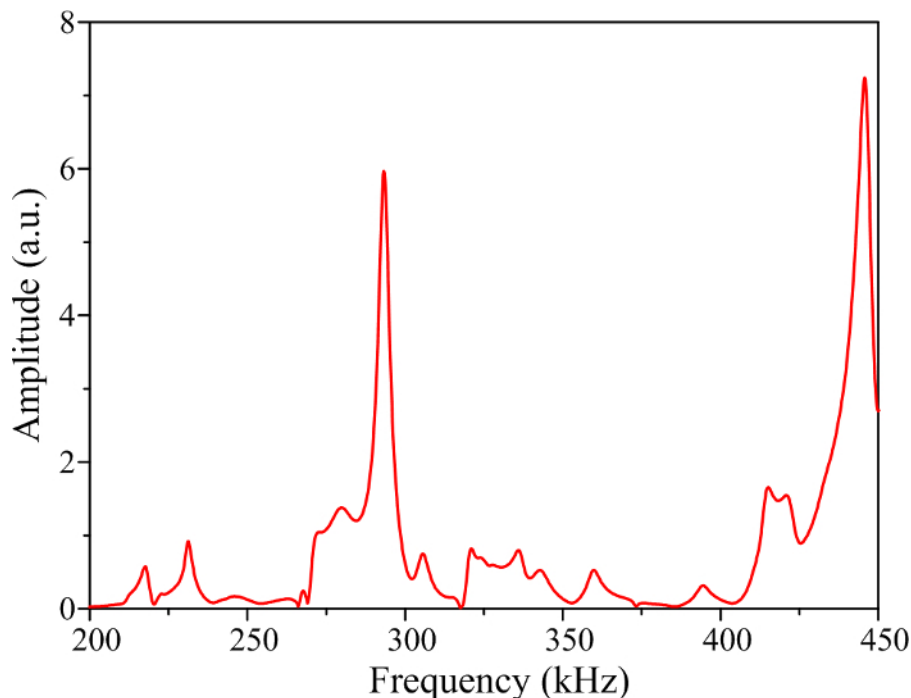


Figure 9: A typical resonant ultrasound spectrum of a PZT-5A sample. The quality factor Q of the PZT-5A sample is about seventy-five¹². Generally speaking, the lower the Q -factor of the sample, the more difficult for mode identification. Generally, the RUS method will not give accurate results when the Q -factor is less than 100. [Please click here to view a larger version of this figure.](#)

Discussion

The RUS technique described here can measure the full set material constants using only one sample, which eliminates errors caused by property variation from sample to sample so that self-consistency can be guaranteed. The method can be used for any solid material with a high

quality factor Q , no matter if they are piezoelectric or not. All other standard characterization techniques require several samples to get the full set data and are difficult to achieve self-consistent data.

It is important to precisely measure the elastic constants c_{11}^E , c_{12}^E and c_{44}^E by the ultrasonic pulse-echo method at room temperature. Otherwise, the mode identification would be very difficult because calculated resonance frequencies of many modes are sensitive to these constants.

The failure of inversion calculations at the initial temperature will lead to the failure of determining the full set constants at higher temperatures because mode identification at the initial temperature is used as the base for mode identification at higher temperatures.

At room temperature, 6 constants out of the 10 constants to be determined can be obtained from the pulse-echo method and the capacitance measurements. Hence, only 4 unknown constants, c_{13}^E , c_{33}^E , e_{31} and e_{33} , need to be estimated in the first round of forward calculation in the RUS procedure. The starting values for these 4 unknowns can be guessed based on other constants already known (in the same order of magnitude). Generally speaking, identifying about 20 modes is easy in the RUS forward process. These 20 modes are easily identified because they are well separated in the resonance spectrum, such as Au-3 and Ag-1 modes in **Figure 3**. Matching these 20 modes by adjusting the input values of these 4 estimated constants will give us a set of more accurate guessed values. Then, more number of modes can be identified by matching the calculated frequencies with those measured ones using better guessed input values. Finally, by using more number of identified modes, more accurate values of c_{13}^E , c_{33}^E , e_{31} and e_{33} can be refined by the backward process in the RUS method.

To reduce random fluctuations in the measured data, the temperature dependence of measured resonance frequencies corresponding to each mode was fitted to a polynomial function. Note that there must be an adequate number of modes measured to ensure the accuracy of the inversion results. From experience, the number of resonance frequencies measured should be at least 5 times the number of material constants to be determined¹³.

This protocol describes the procedure of determining the temperature dependence of the full matrix material constants by the RUS technique, using PZT-4 ceramic as an example. The focus here is on the procedure of the RUS technique, not the measured results of PZT-4¹⁰.

The temperature range of the setup is limited by the temperature endurance of the electric wires and the transducers inside the furnace. This technique might be used at even higher temperatures if the sample is held by two buffer rods and the acoustic signal is sent and received through the buffer rods. In that case, electric wires and transducers will be outside of the furnace to avoid heating.

In principle, this RUS technique can be used on any type of solid material so long as it has a high mechanical Q -value (>100). For low Q -value materials, there is peak overlapping problem, making it hard to identify the resonance frequencies as shown in **Figure 9**.

Disclosures

Authors have nothing to disclose.

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