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# High temperature measurement and characterisation of piezoelectric properties.

P.M. Weaver<sup>1 a</sup>, T. Stevenson<sup>2</sup>, T. Quast<sup>3</sup>, G. Bartl<sup>3</sup>, T. Schmitz-Kempen<sup>4</sup>, P. Woolliams<sup>1</sup>, A. Blumfield<sup>1</sup>, M. Stewart<sup>1</sup>, M.G. Cain<sup>1</sup>

<sup>1</sup> National Physical Laboratory, Teddington, TW11 0LW, UK

<sup>2</sup> Institute for Materials Research, University of Leeds. Leeds. LS2 9JT, UK.

<sup>3</sup> Physikalisch-Technische Bundesanstalt, Braunschweig und Berlin, Germany.

<sup>4</sup> aixACCT Systems GmbH, 52068 Aachen, Germany.

<sup>a</sup> corresponding author; tel +44(0) 20 8943 6228, email paul.weaver@npl.co.uk

## Abstract

Currently available high performance piezoelectric materials, predominantly based on lead zirconate titanate (PZT), are typically limited to operating temperatures of around 200 °C or below. There are many applications in sectors such as automotive, aerospace, power generation and process control, oil and gas, where reliable operation at higher temperatures is required for sensors, actuators and transducers. New materials are being actively developed to meet this need. Development and application of new and existing materials requires reliable measurement of their properties under these challenging conditions.

This paper reviews the current state of the art in measurement of piezoelectric properties at high temperature, including direct and converse piezoelectric measurements and resonance techniques applied to high temperature measurements. New results are also presented on measurement of piezoelectric and thermal expansion and the effects of sample distortion on piezoelectric measurements. An investigation of the applicability of resonance measurements at high temperature is presented, and comparisons are drawn between the results of the different measurement techniques. New results on piezoelectric resonance measurements on novel high temperature piezoelectric materials, and conventional PZT materials, at temperatures up to 600 °C are presented.

Keywords: Piezoelectric, High Temperature, Measurement, Metrology, Interferometry

# 1. Introduction

## 1.1 High Temperature Piezoelectric Applications

Piezoelectric materials are used as the active material for sensors, actuators and motors, acoustic and ultrasonic transducers, and energy harvesters. Whilst most current applications are designed for operation at around room temperature, there are major opportunities for piezoelectric technologies that work at higher temperatures. Some potential applications include valves for fuel controls, hydraulic and pneumatic valves and pumps in automotive and aerospace applications, self-powered sensors in aero-engines, and ultrasonic transducers for non-destructive evaluation of power and process plant or down-hole oil and gas surveying.

Actuator applications such as pumps require a maximum stroke from the actuator under the operating load, but for a valve, the positional stability over a wide temperature range must also be taken into account [1].

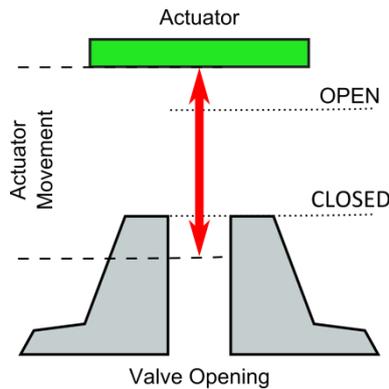


Figure 1: Schematic valve actuator.

The range of movement for an example valve actuator is shown in Figure 1. The actuator movement must be aligned with the valve opening to ensure that the OPEN and CLOSED states can be reached. The positioning of the actuator relative to the valve is affected by thermal expansion which can show complex behaviour in ferroelectrics [2], [3][4][5]. Thermal expansion is also important for reliable device assembly in applications such as high temperature transducers for non-destructive evaluation (NDE) in nuclear power plant where thermal expansion mis-match can lead to de-bonding and device failure [6].

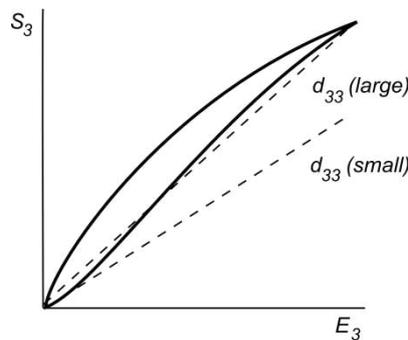


Figure 2 Strain-electric field characteristic of a piezoelectric actuator (schematic).

Another important factor for actuator applications is the effect of electric field. Figure 2 shows the strain response of a piezoelectric actuator to an applied unipolar electric field. The small field piezoelectric coefficient  $d_{33}(\text{small})$  is the slope of the strain-field response at small field. At higher field hysteresis and saturation become more significant, causing deviations in response from the small field limit. Of interest for actuator applications is usually the high field response, expressed by an effective coefficient at high field,  $d_{33}(\text{large})$ . This will depend on the amplitude of the field. At low temperature the available movement may be restricted by hysteresis, whilst at high temperature, saturation in the strain-field characteristic can limit actuator stroke [1].

For ferroelectric ceramic piezoelectrics such as PZT, upper temperature limits are set by the presence of phase transitions and increasing conductivity of the material [7]. The Curie temperature of a ferroelectric is associated with a transition to a paraelectric phase which does not exhibit piezoelectricity [8]. However, piezoelectric properties are diminished well below this temperature due to partial depoling. This is a major constraint for sensors and transducers, but high field actuation can be observed up to or even above the Curie temperature where the response is electrostrictive rather than piezoelectric [3]. Undoped PZT is known as a wide band gap semiconductor with a band gap of between 2.6 eV and 3.5 eV [9]. Thermally activated processes associated with defects and vacancies also give rise to conductivity in the material [10]. At room temperature, this is not usually significant but as the temperature increases, the conductivity increases rapidly. High conductivity can limit the electric field that can be applied without dissipating excessive power. In high power transducers and actuators this can contribute, alongside dielectric losses, to temperature rise or device failure [11][12]. For sensor and energy harvesting applications, electric field strengths are generally low. However, high conductive losses will diminish the effectiveness of energy harvesters and sensors, and result in a small RC time constant, restricting the frequency range over which a sensor or transducer can be used. As well as placing practical limitations on device operation, conductive losses can also have a strong influence on the measurement process, coupling into dielectric measurements through interfacial polarisation, and self-heating causing discrepancies between the temperature of the sample environment and the actual sample temperature.

## 1.2 High Temperature Piezoelectric Measurement Techniques

Techniques appropriate for high temperature measurements fall mostly into three basic categories:

1. Direct piezoelectric effect: measuring charge or voltage resulting from the application of a mechanical deformation to a piezoelectric material. A common room temperature method is the Berlincourt method [13][14][15] where the charge is measured resulting from an oscillating mechanical force. There are few reports of the use of this technique at elevated temperatures [16].
2. Converse piezoelectric effect: measurement of piezoelectric strain resulting from the application of an electric field to a piezoelectric material. This method is more widely reported using a variety of strain measuring techniques.
3. Piezoelectric resonance: because piezoelectric materials couple electrical and mechanical energies, mechanical resonances can be measured electrically and their frequencies used to calculate piezoelectric material properties [17]. Room temperature application of the method has been standardised [18], [19]. Because this measurement can be performed with only electrical access to the test specimen, it is more widely used for measurement at elevated temperature.

X-ray and neutron diffraction should also be mentioned as complementary techniques for measuring piezoelectric properties. Whilst these techniques don't directly measure the piezoelectric effect, they are powerful tools for gaining information on strain in the crystal lattice and phase transitions [20], and the contributions of domain wall motion [21] and domain switching [22] to the piezoelectric coefficients. Diffraction studies of piezoelectric materials at temperatures up to 500 °C have helped understand the relationship between polarisation changes, piezoelectric properties and structural transformations in bismuth ferrite – lead titanate and related ceramics [23].

Whilst some authors have performed “reasonableness” checks on their measurements such as comparison with manufacturers' data sheets, there has been no structured attempt to validate the various measurement techniques used for high temperature piezoelectric measurement, or to compare results of different measurement techniques.

This paper describes the implementation of four separate measurement systems: full optical field interferometry capable of measuring the expansion and surface profile of a sample up to 200 °C, single beam interferometry with DC capability up to 600 °C, commercial single and double beam interferometry through a contact piece up

to 800 °C and resonance measurement up to 800 °C. Initial results from the various techniques are compared, and possible artefacts affecting measurement results are discussed.

### 1.3 Measurement of the Converse Piezoelectric Effect at High Temperature

This technique measures the expansion (or contraction) resulting from the application of an electric field to the piezoelectric material. This lends itself to assessment of the actuating capabilities of a material at high electric field, but values for piezoelectric coefficient in the low field limit, also provide information on sensing and transducer-related properties.

The piezoelectric expansion can be measured by transmission of the movement through a pushrod to an external position sensor, typically a linear variable differential transformer (LVDT). This is the operating principal of most commercial pushrod dilatometers. This type of system can offer high resolution over a wide temperature range and provides static or low frequency measurement which may include thermal expansion. However, careful calibration is required to minimise the effects of differential thermal expansion of the rods which pass through a steep temperature gradient between the heated zone and the sensor. This is particularly problematic for non-static measurements where steady state thermal conditions cannot be realised. This type of measurement is not suited to frequencies above a few mHz. Pushrod dilatometers have been used to measure the coupling between piezoelectric and thermal expansion and their relation to electrostriction and charge control of actuation in soft PZT up to 200 °C [2], [3] as well as straightforward thermal expansion measurement [5] (the latter using a capacitive sensor). A pushrod / LVDT arrangement, in combination with an external load sensor was used to measure both stress and strain at temperatures up to 150 °C, allowing assessment of the work output of an actuator at elevated temperature [24].

Optical techniques such as interferometry can offer the advantages of high accuracy, direct measurement of the movement, high frequency capability, and traceability of measurement. Unlike pushrod systems, they can provide a direct measurement of length or length change without the need for calibration against reference samples.

Interferometry uses interference between a light beam or beams reflecting from the sample surface and a reference beam to measure changes in the optical path length as a piezoelectric sample expands or contracts. Single beam interferometer systems measure deflection of one surface only, while a dual beam system measures both front and back surfaces to minimise common mode expansion or effects due to sample distortion, especially in thin films [25] [26]. Commercial systems are available (e.g. aixACCT systems) that offer single and double beam laser interferometer measurement of a piezoelectric displacement of a sample held between two contact pieces. The sample environment can be heated or cooled. Reported in this paper are advances which have made possible the extension of the temperature range of the aixACCT system up to 600 °C. Commercial double-beam laser interferometer systems measure non-contact deflections in the sub-pm range on thin films or on bulk materials at low field. These systems do not measure “DC” effects such as thermal expansion. There are also reports of laser dilatometer type systems [27] used to measure thermal expansion in piezoelectric devices. Combined measurements of thermal and piezoelectric expansion using a pushrod dilatometer have been reported [2], [3] but these measurements are restricted to very low frequencies (<0.1 Hz) and subject to the limitations of pushrod dilatometers especially for dynamic measurements. We are not aware of any reports of simultaneous measurement of DC thermal and piezoelectric expansion as well as high frequency piezoelectric motion.

A related optical technique is laser Doppler vibrometry (LDV) which detect the shift in frequency of a laser beam reflected from a moving surface. This technique, particularly suited to higher frequency measurements, can be adapted for measurement of piezoelectric movement at high temperature. Examples of the use of this technique include LDV measurements at 1 kHz of piezoelectric  $d_{33}$  coefficients at temperatures up to 500 °C which were correlated with temperature-dependent XRD measurements [23] and measurement of the response

of piezoelectric composites in the range 0.1-10 kHz at more moderate temperatures between -50 °C and +50 °C [28]

## 1.4 High Temperature Piezoelectric Resonance

Piezoelectric resonance is a widely used method for obtaining small field piezoelectric coefficients [21][18][19]. It requires the preparation of a set of samples with different geometries to isolate the different piezoelectric resonance modes and can be used to derive a full set of piezoelectric coefficients, elastic and electrical compliances. The methods described in the standards are based on the assumption that the electrical and mechanical losses are negligible. As discussed above, as the temperature increases, piezoelectric materials become more conductive. At high temperature, particularly for ferroelectric and related perovskite materials, the losses due to conductivity can be very significant and the assumption of negligible loss is no longer valid. There has been a significant amount of work done to develop models for resonance in lossy piezoelectrics, usually by treating the piezoelectric, elastic and electrical coefficients as complex coefficients where the imaginary part represents the loss [29][30][31][32], [33] (techniques including PRAP reviewed by Kwok [34]). A computerised version of the complex coefficients model has been implemented in commercial software PRAP (<http://www.tasitechnical.com>), and there also exist implementations that are freely available ([www.piezoinstitute.com/resources/tools/](http://www.piezoinstitute.com/resources/tools/)) [32], [33].

Because of the convenience of an electrical measurement with no requirement for mechanical or optical access to the sample, resonance has been more widely used for high temperature piezoelectric characterisation than other methods. Resonance measurements have been reported at temperatures up to 1400 °C for a variety of materials including lead titanate based relaxors up to 150 °C [35], commercial lead- and bismuth- based ceramics up to 500 °C [36], lithium-sodium niobate ceramics up to 800 °C [37], ordered langasite crystals up to 900 °C [38], rare earth calcium oxyborate single crystal (YCOB) up to 950 °C [39] and 1000 °C [40], langasite and  $\alpha$ -quartz crystals up to 1400 °C [41][42]. For high quality crystals at moderate temperatures, the standard (low loss) method can be applied directly with no account taken of the effects of the losses, but this is unlikely to be the case particularly for many perovskite lead and bismuth based piezoelectrics even at moderately elevated temperatures.

Complex coefficient loss models have been developed to account for losses in a generic way, not explicitly for high temperature measurement. At high temperature, the loss is associated primarily with conductivity, rather than dielectric loss, and there have been proposals to extend the lossy model, for instance, by including a bulk parallel resistance in an extended Butterworth-van Dyke equivalent circuit model [41] [42].

## 1.5 Piezoelectric materials for high temperature applications

Ferroelectric ceramics are in widespread use as sensors, actuators and transducers with lead zirconate titanate (Pb,Zr)TiO<sub>3</sub> (PZT) and related materials dominating commercial piezoelectrics. These materials combine high electromechanical coupling, low cost and flexibility in shape and composition resulting from the ceramic processing used in their fabrication. Whilst these materials do provide a wide operating temperature range, they are not suitable for high temperature applications that approach or exceed the Curie temperature ( $T_C$ ). Most commercial PZT ceramics have at  $T_C$  of between 300 °C and 400 °C, and a generally recommended maximum operating range is up to half  $T_C$  in Celsius, although for high field actuator type application, significant electro-mechanical activity (electrostrictive) can be observed above  $T_C$  [3]. There currently exist a number of materials suitable for high temperature piezoelectric devices [7][43][44][45][46] (see also companion paper in this edition [47]), but generally, piezoelectric coupling reduces as the maximum operating temperature (or  $T_C$  for ferroelectrics) decreases [43]. This has led to the investigation and use of novel perovskite ceramics based on

the BiFeO<sub>3</sub> – PbTiO<sub>3</sub> system [48] as a high temperature, high activity material that can be manufactured using conventional mixed oxide techniques, and at similar cost. There is also a need for high activity reference materials, and a high T<sub>C</sub> material has the potential to provide stable performance over a wide temperature range.

The results presented in this paper used commercially available PZT (Noliac NCE80) and high temperature piezoelectric KBT-BFPT with composition details described in [49].

## 2. Results and Discussion

### 2.1 High Temperature Resonance

Resonance measurements were performed using a TA Instruments Q400 thermo-mechanical analyser (TMA), which maintained a steady ramp rate of 2°C min<sup>-1</sup> (capable up to 1000 °C). The TMA was modified to provide electrical connections into the furnace with 1 mm diameter platinum spheres making contact with the sample electrode. Impedance sweeps were performed using an Agilent 4294a precision impedance analyser over a range of 300 kHz– 800 kHz. The impedance analyser was connected to the TMA by an Agilent 16048H 2 m port extender. Temperature was controlled by a thermocouple placed in close proximity to the sample. A temperature calibration of the modified furnace was carried out using dummy samples made of Inconel with calibrated thermocouples welded to their surface. Open circuit and short circuit impedance measurements were made over the frequency range of interest prior to the temperature run. Separate open and short circuit measurements across the full temperature range verified that there was no significant change with temperature. Open and short circuit impedance measurements were used to apply compensation for the parasitic impedances associated with the custom made test fixture and the cabling.

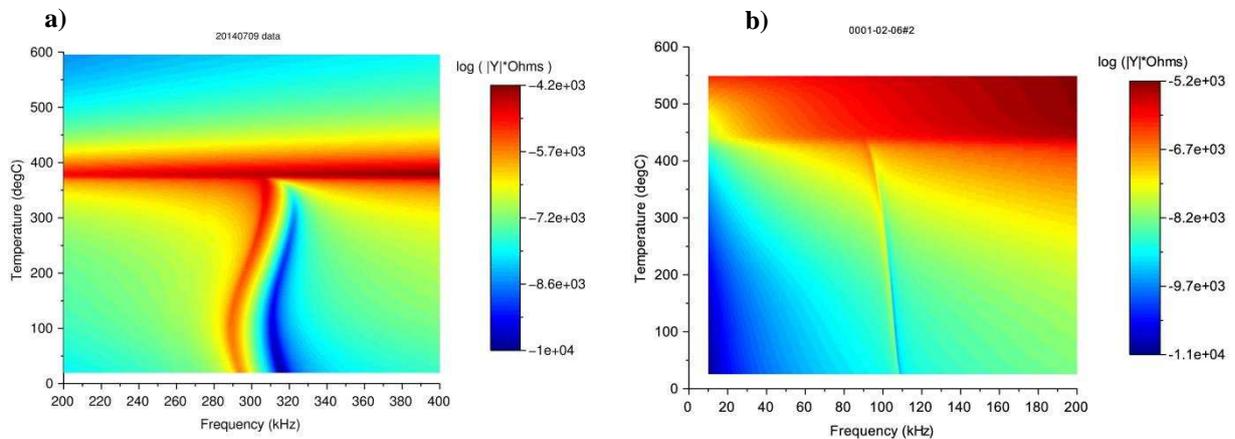


Figure 3 Impedance spectra for a) PZT (Morgan PZT5A4), b) KBT-BFPT (composition A [49]) colour mapped as functions of frequency and temperature.

Results are shown in Figure 3 for a commercial PZT (Morgan PZT5A4) and a high temperature material, (K Bi)TiO<sub>3</sub> – BiFeO<sub>3</sub> – PbTiO<sub>3</sub> (KBT-BFPT), developed at the University of Leeds [49]. The resonance and anti-resonance are clearly seen in both sets of spectra, with a cut-off at the Curie temperature. For the PZT sample the Curie temperature is 377 °C, compared to a datasheet value of 367 °C. For the KBT-BFPT material the temperature at which the piezoelectric resonance disappears is around 450 °C

The standard EN50324 specifies equations to calculate piezoelectric coefficients from peaks in the resonance spectra and is valid for low loss materials. At high temperature conductive losses become significant, causing discrepancies between the EN50324 evaluation and lossy models. In a low loss system it is accurate enough to

evaluate resonance and anti-resonance from the amplitude of the impedance  $|Z|$  but for lossy materials, these peaks can be analysed in a number of different ways according to Table 1 [50] and Figure 4.

**Table 1** Definitions of frequencies  $f_a, f_r, f_s, f_p, f_m, f_n$  [50]

$f^{(1)}$			$f^{(2)}$		
$f_m$	Maximum absolute admittance	Max ( $ Y $ )	$f_n$	Maximum absolute impedance	Max ( $ Z $ )
$f_s$	Maximum conductance	Max (Re( $Y$ ))	$f_p$	Maximum resistance	Max (Re( $Z$ ))
$f_r$	Zero susceptance	Im( $Y$ )=0	$f_a$	Zero reactance	Im( $Z$ )=0

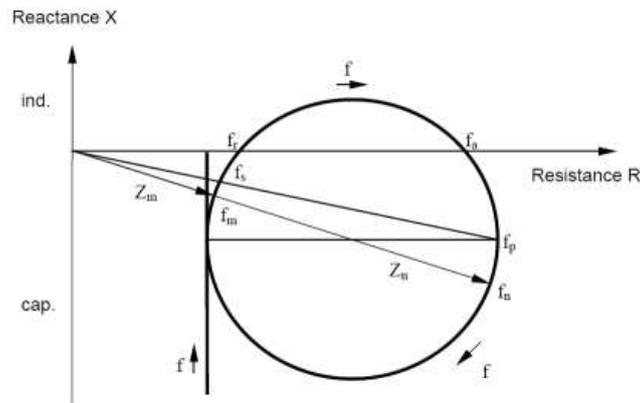


Figure 4 Schematic Impedance plot showing frequencies  $f_a, f_r, f_s, f_p, f_m, f_n$

For a low loss material  $f_1 \approx f_m \approx f_s \approx f_r$  and  $f_2 \approx f_n \approx f_p \approx f_a$  but for a lossy material these values diverge as shown in Figure 5.

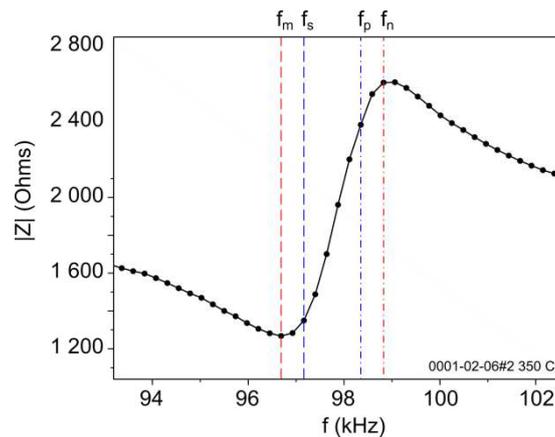


Figure 5 Resonance spectrum for KBT-BFPT (composition A [49]) at 350°C showing divergence of frequencies  $f_m, f_n, f_s, f_p$

This shows that simple application of the standard low loss model can be subject to large errors in high temperature measurements with significant conductivity present. This is likely to be the case if peaks are measured from the maxima and minima in amplitude of the impedance  $|Z|$  - a measurement which can be made using simple equipment as described in EN50324 [18]. However, modern impedance analysers can easily

transform between impedance and admittance planes allowing evaluation of peaks in admittance, impedance, conductance and resistance to obtain  $f_s$ ,  $f_p$ ,  $f_m$ ,  $f_n$ .

Obtaining values of  $f_a$ ,  $f_r$  (where the loop crosses the  $X=0$  axis) is more difficult as they are strongly affected by the loss (Figure 6).

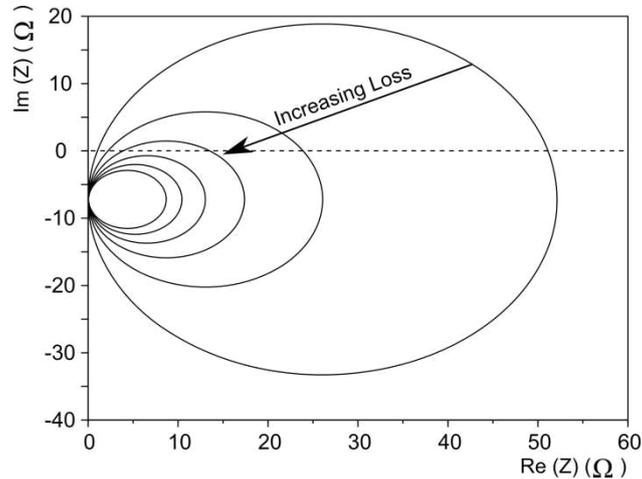


Figure 6 Effect of increasing loss on impedance spectra in the complex plane.  $f_a$  and  $f_r$  resonant and anti-resonant frequencies are defined as the frequencies where the line crosses the  $\text{Im}(Z)=0$  axis and are therefore strongly affected by loss.

The effect of the choice of frequency pair on the coupling coefficient and charge coefficient are shown in Figure 7. Using the  $(f_m, f_n)$  frequency pair (approximately equivalent to using maximum and minimum of  $|Z|$ ) leads to significant errors in the coupling ( $k$ ) and piezoelectric coefficient ( $d$ ). However, using the  $(f_s, f_p)$  frequency pair gives reasonable agreement with PRAP for the coupling ( $k$ ). The larger deviation in  $d$  is caused by differences in the permittivity evaluated by the two methods. A significant factor is the frequency dependence of the capacitance. At high temperature conductivity contributes to the permittivity through interfacial (Maxwell-Wagner) polarisation leading to strong frequency dependence of the capacitance, especially at low frequency. This is still a strong influence at 1 kHz – the frequency recommended in EN50324 for the evaluation of the capacitance.

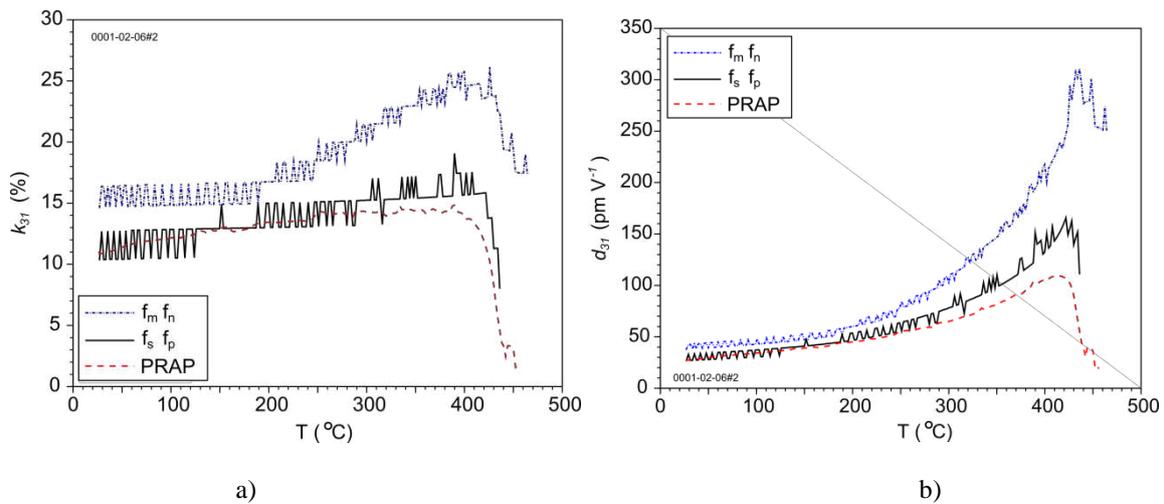


Figure 7 a)  $k_{31}$  and b)  $d_{31}$  for KBT-BFPT (composition A [49]) evaluated using  $(f_m, f_n)$ ,  $(f_s, f_p)$  and PRAP.

This implies that lossless model in EN50324 can produce results close to those of a lossy model by using  $f_s$  and  $f_p$  rather than maxima and minima in  $|Z|$ , and evaluating the permittivity away from the highly frequency dependent low frequency region. As long as this can be done sufficiently below resonance, it should still meet the approximation to zero stress conditions. A limitation of all of these models, including the lossy models, is that it is assumed that all properties are frequency independent.

## 2.2 High Temperature Jamin Interferometer

The main objective for this system was to produce highly traceable  $d_{33}$  piezoelectric charge coefficient measurements combined with thermal expansion measurement at high temperature. The system is configured as a dual beam Jamin interferometer [51] (Figure 8) to exploit the fundamental link between the laser wavelength and the change in height of the upper sample surface when an electric field is applied to a piezoelectric sample. The interferometer measures changes in the beam path length between the top surface of the sample and the reference block, enabling evaluation of length changes in the sample due to piezoelectric and thermal strains. The dual beam configuration makes the interferometer largely immune to common mode effects such as vibration while the double pass arrangement on both the reference and the sample beams largely eliminates the effects of tilt. The system is built into a vertical vacuum furnace capable of operating up to 1000 °C with optical and electrical access.

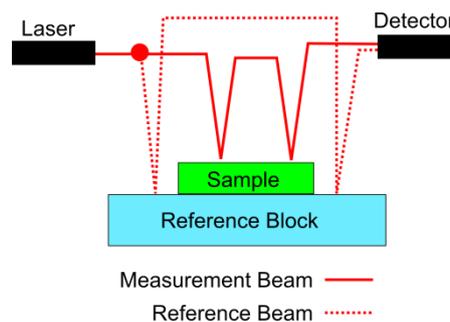


Figure 8 Schematic of the Jamin interferometer with relation to the sample and reference platform

The maximum temperature of the system in vacuum is currently limited to 600 °C. This limitation is mainly due to the specialist Ti-Au and Pt coatings (required for reflectivity and electrical conductivity on the sample and reference block) degrade rapidly beyond this temperature. The coatings must remain reflective and stable to ensure that an interferogram signal can be obtained. Measurements are conducted in vacuum to minimise convection effects occurring between the Jamin interferometer head and the top of the furnace chamber, and to eliminate uncertainties due to the lack of precise knowledge of the refractive index of air at elevated temperatures. The sample and reference measurement beams in the interferometer need to be parallel. This requires the samples to be polished with a very high degree of flatness and parallelism between the two main faces. Measurements are conducted on highly polished 15mm diameter, 2mm thick discs, with <30nm flatness and <4 arc-second parallelism. The main faces are coated with an electrically conductive and optically reflective coating of Ti: Au or Pt using thermal evaporation of sputter coating with Pt electrodes.

Figure 9 shows the results of a thermal expansion measurement at zero electric field (short circuit) on a commercial PZT (Noliac NCE80). On the initial heating, the sample contracts producing a negative thermal expansion. This phenomenon has been observed previously [4][5] and is a consequence of the piezoelectric coupling to the thermal depolarisation. Thermal expansion measurements were validated by performing measurements on a parallel polished 2 mm thick silicon disc sample with a 15 mm diameter. The results were in close agreement with silicon thermal expansion reference data [52].

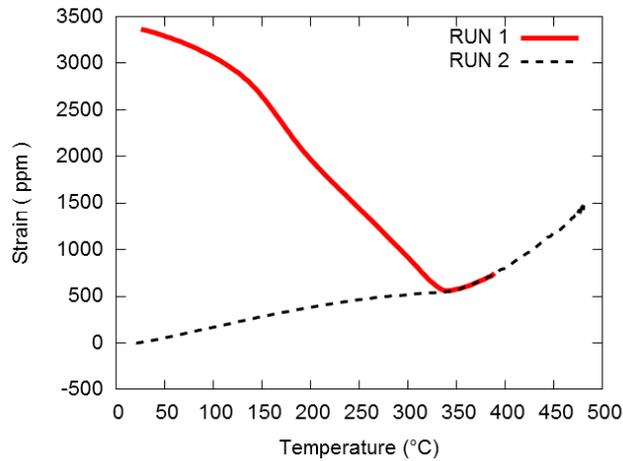


Figure 9 Thermal expansion at zero electric field in PZT (Noliac NCE80)

Figure 10 shows piezoelectric displacement of a commercial hard PZT (NCE80) at different temperatures, showing an increase in the effective  $d_{33}$  coefficient with temperature.

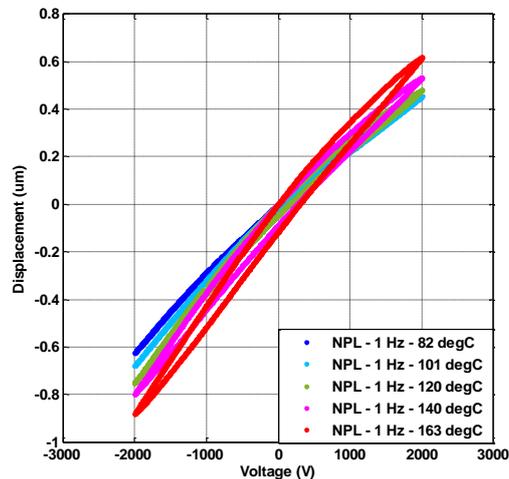


Figure 10 Jamin interferometer measurements on PZT (Noliac NCE80)

### 2.3 High Temperature Commercial Single Beam Interferometer

Large field piezoelectric displacement was measured using a piezoelectric evaluation system (aixPES) from aixACCT with a modified sample environment capable of elevated temperature measurements up to 800 °C (Figure 11). Displacement was measured using a single beam laser interferometer while electrical response was simultaneously recorded using virtual ground current measurement. This allows AC and DC, large and small field characterisation to be performed within one temperature cycle. Resonance measurements are also possible using the same system. Figure 12 shows high field measurements on the same PZT samples, but at higher field in comparison to the above measurements. These show similar behaviour to results obtained with the Jamin interferometer Figure 10



Figure 11 High-temperature sample holder for aixPES system.

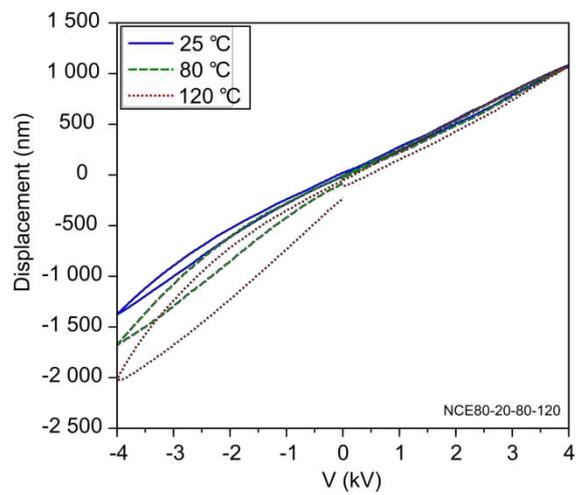


Figure 12 aixPES measurement on PZT (NCE80)

The same sample holder has been used to measure high temperature materials in Figure 13 below.

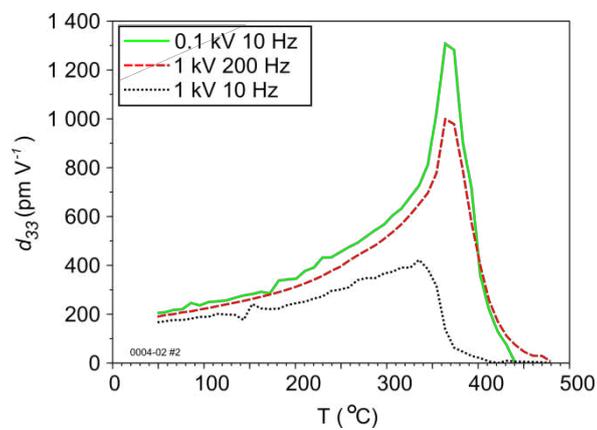


Figure 13  $d_{33}$  from aixACCT aixPES for composition E1 [49]. Large-signal: 1 kV unipolar 10 Hz, small-signal 100 V amplitude bipolar, measured within in the same temperature sweep.

Figure 13 shows the effective piezoelectric coefficient obtained from the aixACCT aixPES for sample composition E1 [49]. The small signal results are comparable to the resonance data (**Error! Reference source not found.**), but a very large peak in the piezoelectric strain is observed at 364 °C under large signal conditions, followed by a rapid drop in effective  $d_{33}$ .

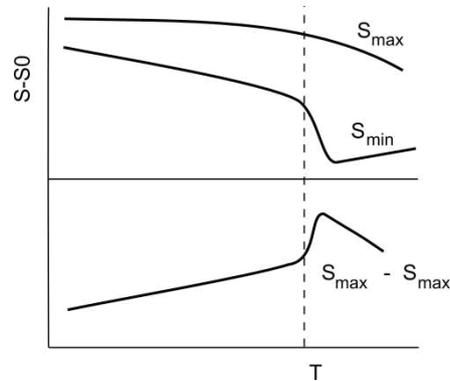


Figure 14 Schematic of strain at high field ( $S_{max}$ ) and zero field ( $S_{min}$ ) and the difference between them as a function of temperature.

Figure 14 shows schematically the thermal and piezoelectric strain at zero field,  $S_{min}$ , and high field,  $S_{max}$ , relative to the strain at a reference temperature,  $S_0$ . The zero field remanent strain,  $S_{min}$ , which is coupled piezoelectrically to the remanent polarisation, drops rapidly at the transition temperature, but the strain at high field persists [3], resulting in a peak in the strain difference and therefore the large signal piezoelectric response. The high temperature materials reported here have high crystal  $c/a$  ratio [49][53] and therefore this effect will be particularly pronounced and may explain the very large piezoelectric displacements observed here (in excess of  $1000 \text{ pm V}^{-1}$ ) in Figure 13.

## 2.4 Full-field Multi-wavelength phase-shifting interferometry

Multi-wavelength phase-shifting interferometry was used to measure strain maps of the complete sample surface with high accuracy using the PTB (Physikalisch-Technische Bundesanstalt) ultraprecision interferometer (UPI) [54] with a sample environment which allows one to heat the sample (up to 200 °C) and to apply an electric field (Figure 15).

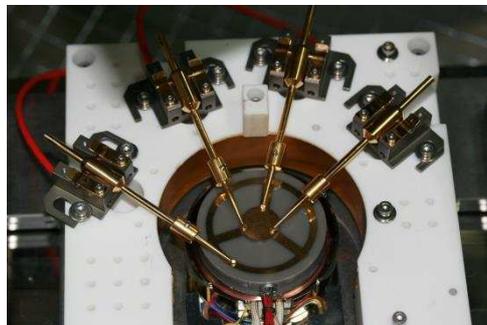


Figure 15 Sample environment for phase-shifting interferometry

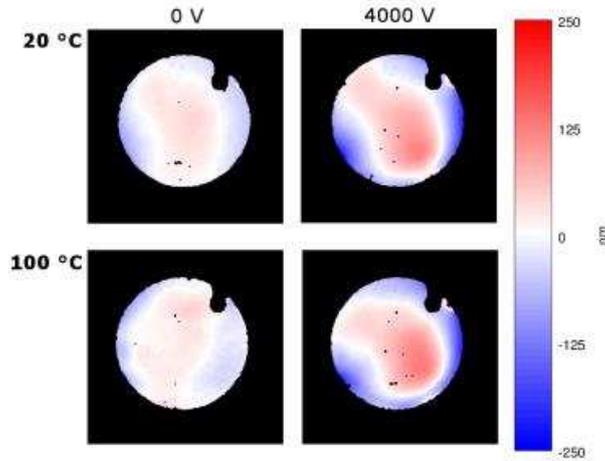


Figure 16 Relative height variation in nanometres across the top surface (bias length and tilt subtracted) at 20 °C (top row) and 100 °C (bottom row). Voltage-dependent deformations at 2 kV mm<sup>-1</sup> are shown in the right column.

Absolute length change measurements were evaluated at room temperature and 100 °C using a commercial PZT sample. An absolute length map of the sample surface is shown in Figure 16 as a surface plot of the extremities (0 V mm<sup>-1</sup> and 2 kV mm<sup>-1</sup>) for 20 °C and 100 °C. By calculating the absolute length evaluated as an average over the entire sample area for each frame, a strain-field relationship can be drawn, and is shown in Figure 17, compared to data from the aixACCT system. For better comparability, the absolute length of the sample is treated as an offset and subtracted.

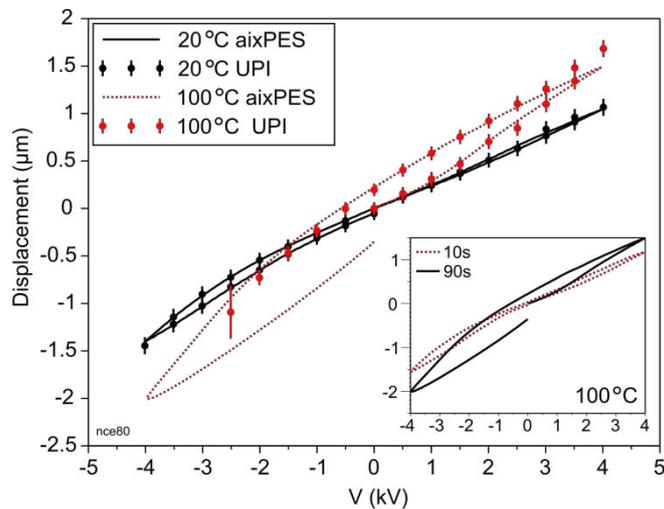


Figure 17 Length change (displacement) of a PZT sample (Noliac NCE80) for different applied voltages (bipolar up to +/- 2 kV mm<sup>-1</sup>) for 20 °C and 100 °C measured by UPI (dots) and aixACCT commercial single beam system (lines). Inset shows the effect of time at 100 °C using data from the aixPES after 10 s and 90 s of applied field at 0.1 Hz.

Figure 17 shows that close agreement can be obtained if the measurement conditions are comparable [46], particularly the stabilisation time at temperature and the duration of the electric field application. The UPI applies the field for a significant time (90 s) to obtain the measurement. Applying a similar stabilisation time using the aixACCT system provided comparable results at 100 °C, although room temperature results were not affected.

### 3. Conclusions

Whilst techniques for the measurement of piezoelectric properties at room temperature are well established, their application to evaluation of properties at high temperature presents many challenges. This paper presents an overview of measurement techniques adopted for high temperature measurements which are based primarily on the converse piezoelectric effect (displacement measurement under applied electric field), the direct piezoelectric effect (charge or voltage measurement under applied stress), or low field piezoelectric resonance. Piezoelectric resonance provides the convenience of a purely electrical measurement of electro-mechanical coupling, but requires a model to obtain piezoelectric coefficients from the measured data. Significant errors can result if the model and the analysis do not take into account the high temperature conditions, particularly sample conductivity. Other techniques include various strain measuring techniques and Berlincourt methods. Thermal expansion, and its coupling to piezoelectric strain is important in many applications, particularly for ferroelectric ceramics, but many techniques provide no information on this.

A combination of measurement facilities is presented which provides unique capability for the measurement of static and dynamic piezoelectric properties across a wide temperature range, including the coupling to thermal expansion. Absolute length measurements with full optical field mapping of the piezoelectric sample shows that sample distortion can be significant and may influence single point measurements. For higher temperatures the resonance and single beam interferometer systems provide complementary measurements but neither provides data on the high temperature coupling between thermal expansion and piezoelectric displacement. A non-contact interferometer system is described which provides coupled piezoelectric / thermal expansion measurements up to 600 °C. Measurements on novel BF-PT piezoelectric materials have shown large piezoelectric displacement at temperatures in excess of 400 °C, for both small field and large field coefficients. It is shown that effects such as duration of application of electric field can have a significant effect on piezoelectric properties, and care is needed to ensure comparable measurement conditions and control of the experiment to obtain reliable results.

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### 5. References

- [1] P. M. Weaver, “A sensorless drive system for controlling temperature-dependent hysteresis in piezoelectric actuators,” *Ultrasonics, Ferroelectrics and Frequency Control*, IEEE Transactions on, vol. 58, no. 4, pp. 704–710, Apr. 2011.
- [2] P. M. Weaver, M. G. Cain, and M. Stewart, “Temperature dependence of strain–polarization coupling in ferroelectric ceramics,” *Applied Physics Letters*, vol. 96, no. 14, p. 142905, 2010.
- [3] P. M. Weaver, M. G. Cain, and M. Stewart, “Temperature dependence of high field electromechanical coupling in ferroelectric ceramics,” *Journal of Physics D: Applied Physics*, vol. 43, no. 16, p. 165404, 2010.
- [4] W. R. Cook, D. A. Berlincourt, and F. J. Scholz, “Thermal Expansion and Pyroelectricity in Lead Titanate Zirconate and Barium Titanate,” *Journal of Applied Physics*, vol. 34, no. 5, pp. 1392–1398, 1963.

- [5] S. Kallaev, G. Gadzhiev, I. Kamilov, Z. Ornarov, S. Sadykov, and L. Reznichenko, "Thermal properties of PZT-based ferroelectric ceramics," *Physics Of The Solid State*, vol. 48, no. 6, pp. 1169–1170, Jun. 2006.
- [6] M. Budimir, A. Mohimi, C. Selcuk, and T.-H. Gan, "High temperature nde ultrasound transducers for condition monitoring of superheated steam pipes in nuclear power plants," in *Proceedings of the International Conference Nuclear Energy for New Europe*, Bovec, Slovenia, 2011.
- [7] D. Damjanovic, "Materials for high temperature piezoelectric transducers," *Current Opinion in Solid State and Materials Science*, vol. 3, no. 5, pp. 469–473, 1998.
- [8] M. Lines and A. Glass, *Principles and Applications of Ferroelectrics and Related Materials*. Clarendon, Oxford, 1977.
- [9] B. Nagaraj, S. Aggarwal, T. Song, T. Sawhney, and R. Ramesh, "Leakage current mechanisms in lead-based thin-film ferroelectric capacitors," *Physical Review B*, vol. 59, no. 24, pp. 16022–16027, 1999.
- [10] B. Jaffe, W. . Cook, and H. Jaffe, *Piezoelectric ceramics*. Academic Press, 1971.
- [11] M. Stewart and M. G. Cain, "Measurement and modelling of self-heating in piezoelectric materials and devices," in "Characterisation of Ferroelectric Bulk Materials and Thin Films" ed. MG Cain, Springer, 2014, pp. 147–189.
- [12] S. Zhang, R. Xia, L. Lebrun, D. Anderson, and T. R. Shroud, "Piezoelectric materials for high power, high temperature applications," *Materials letters*, vol. 59, no. 27, pp. 3471–3475, 2005.
- [13] M. Stewart and M. Cain, "Direct Piezoelectric Measurement: The Berlincourt Method," in "Characterisation of Ferroelectric Bulk Materials and Thin Films" ed. MG Cain, Springer, 2014, pp. 37–64.
- [14] D. Damjanovic, "Stress and frequency dependence of the direct piezoelectric effect in ferroelectric ceramics," *Journal of applied physics*, vol. 82, no. 4, pp. 1788–1797, 1997.
- [15] A. Barzegar, D. Damjanovic, and N. Setter, "The effect of boundary conditions and sample aspect ratio on apparent  $d_{33}$ /piezoelectric coefficient determined by direct quasistatic method," *Ultrasonics, Ferroelectrics, and Frequency Control, IEEE Transactions on*, vol. 51, no. 3, pp. 262–270, 2004.
- [16] M. Davis, D. Damjanovic, and N. Setter, "Temperature dependence of the direct piezoelectric effect in relaxor-ferroelectric single crystals: Intrinsic and extrinsic contributions," *Journal of applied physics*, vol. 100, no. 8, p. 084103, 2006.
- [17] M. Cain and M. Stewart, "Piezoelectric Resonance," in "Characterisation of Ferroelectric Bulk Materials and Thin Films" ed. MG Cain, Springer, 2014, pp. 15–36.
- [18] CENELEC, EN 50324-2:2002 Piezoelectric properties of ceramic materials and components - Part 2: Methods of measurement and properties - low power. CENELEC, 2002.
- [19] Meeker, "Publication and Proposed Revision of ANSI/IEEE Standard 176-1987 "ANSI/IEEE Standard on Piezoelectricity," *Ultrasonics, Ferroelectrics and Frequency Control, IEEE Transactions on*, vol. 43, no. 5, p. 717, Sep. 1996.
- [20] J. Wooldridge, S. Ryding, S. Brown, T. L. Burnett, M. G. Cain, R. Cernik, R. Hino, M. Stewart, and P. Thompson, "Simultaneous measurement of X-ray diffraction and ferroelectric polarization data as a function of applied electric field and frequency," *Journal of Synchrotron Radiation*, vol. 19, no. 5, pp. 0–0, 2012.
- [21] A. Pramanick, D. Damjanovic, J. E. Daniels, J. C. Nino, and J. L. Jones, "Origins of electro-mechanical coupling in polycrystalline ferroelectrics during subcoercive electrical loading," *Journal of the American Ceramic Society*, vol. 94, no. 2, pp. 293–309, 2011.
- [22] J. Jones, M. Hoffman, J. Daniels, and A. Studer, "Direct measurement of the domain switching contribution to the dynamic piezoelectric response in ferroelectric ceramics," *Applied Physics Letters*, vol. 89, no. 9, p. 092901, 2006.
- [23] T. Leist, J. Chen, W. Jo, E. Aulbach, J. Suffner, and J. Roedel, "Temperature Dependence of the Piezoelectric Coefficient in BiMeO<sub>3</sub>-PbTiO<sub>3</sub> (Me= Fe, Sc,(Mg<sup>1/2</sup>Ti<sup>1/2</sup>)) Ceramics," *Journal of the American Ceramic Society*, vol. 95, no. 2, pp. 711–715, 2012.
- [24] K. G. Webber, E. Aulbach, and J. Rödel, "High temperature blocking force measurements of soft lead zirconate titanate," *Journal of Physics D: Applied Physics*, vol. 43, p. 365401, 2010.
- [25] S. Sivaramkrishnan, P. Mardilovich, A. Mason, A. Roelofs, T. Schmitz-Kempen, and S. Tiedke, "Electrode size dependence of piezoelectric response of lead zirconate titanate thin films measured by double beam laser interferometry," *Applied Physics Letters*, vol. 103, no. 13, p. 132904, 2013.
- [26] L. Burianova, A. Kopal, and J. Nosek, "Characterization of advanced piezoelectric materials in the wide temperature range," *Materials Science And Engineering B-Solid State Materials For Advanced Technology*, vol. 99, no. 1–3, pp. 187–191, 2003.
- [27] A. Wolff, "Large Signal Resonance and Laser Dilatometer Methods," in *Piezoelectricity*, vol. 114, W. Heywang, K. Lubitz, and W. Wersing, Eds. Springer Berlin Heidelberg, 2008, pp. 445–455.

- [28] K. M. Rittenmyer and P. S. Dubbelday, "Direct measurement of the temperature-dependent piezoelectric coefficients of composite materials by laser Doppler vibrometry," *The Journal of the Acoustical Society of America*, vol. 91, no. 4, pp. 2254–2260, 1992.
- [29] R. Holland, "Representation of dielectric, elastic, and piezoelectric losses by complex coefficients," *Sonics and Ultrasonics, IEEE Transactions on*, vol. 14, no. 1, pp. 18–20, 1967.
- [30] J. G. Smits, "Iterative Method for Accurate Determination of the Real and Imaginary Parts of the Materials Coefficients of Piezoelectric Ceramics," *Sonics and Ultrasonics, IEEE Transactions on*, vol. 23, no. 6, pp. 393–401, Nov. 1976.
- [31] S. Sherrit, "Non-iterative evaluation of the real and imaginary material constants of piezoelectric resonators," *Ferroelectrics*, vol. 134, pp. 111–119, 1992.
- [32] C. Alemany, A. Gonzalez, L. Pardo, B. Jiménez, F. Carmona, and J. Mendiola, "Automatic determination of complex constants of piezoelectric lossy materials in the radial mode," *Journal of Physics D: Applied Physics*, vol. 28, no. 5, p. 945, 1995.
- [33] C. Alemany, L. Pardo, B. Jimenez, F. Carmona, J. Mendiola, and A. Gonzalez, "Automatic iterative evaluation of complex material constants in piezoelectric ceramics," *Journal of Physics D: Applied Physics*, vol. 27, no. 1, p. 148, 1994.
- [34] K. W. Kwok, H. L. W. Chan, and C. L. Choy, "Evaluation of the material parameters of piezoelectric materials by various methods," *Ultrasonics, Ferroelectrics and Frequency Control, IEEE Transactions on*, vol. 44, no. 4, pp. 733–742, 1997.
- [35] F. Li, S. Zhang, Z. Xu, X. Wei, J. Luo, and T. R. Shrout, "Temperature independent shear piezoelectric response in relaxor-PbTiO<sub>3</sub> based crystals," *Applied Physics Letters*, vol. 97, no. 25, p. 252903, 2010.
- [36] S. Sherrit, X. Bao, Y. Bar-Cohen, and Z. Chang, "Resonance analysis of high-temperature piezoelectric materials for actuation and sensing," *Smart Structures and Materials*, pp. 411–420, 2004.
- [37] L. Pardo, L. Duran-Martín, J. Mercurio, N. L., and B. Jiménez, "Temperature behaviour of structural, dielectric and piezoelectric properties of sol-gel processed ceramics of the system LiNbO<sub>3</sub>-NaNbO<sub>3</sub>," *J. Phys. and Chem. Solids*, vol. 58, no. 9, p. 1335, 1997.
- [38] S. Zhang, Y. Zheng, H. Kong, J. Xin, E. Frantz, and T. R. Shrout, "Characterization of high temperature piezoelectric crystals with an ordered langasite structure," *Journal of Applied Physics*, vol. 105, no. 11, pp. 114107–114107, 2009.
- [39] S. Zhang, Y. Fei, B. H. T. Chai, E. Frantz, D. W. Snyder, X. Jiang, and T. R. Shrout, "Characterization of piezoelectric single crystal YCa<sub>4</sub>O(BO<sub>3</sub>)<sub>3</sub> for high temperature applications," *Applied Physics Letters*, vol. 92, no. 20, p. 202905, 2008.
- [40] F. Yu, S. Zhang, X. Zhao, D. Yuan, L. Qin, Q.-M. Wang, and T. R. Shrout, "Dielectric and electromechanical properties of rare earth calcium oxyborate piezoelectric crystals at high temperatures," *IEEE Transactions on Ultrasonics, Ferroelectrics and Frequency Control*, vol. 58, no. 4, pp. 868–873, Apr. 2011.
- [41] H. Fritze, "High temperature piezoelectric materials: Defect chemistry and electro-mechanical properties," *Journal of Electroceramics*, vol. 17, no. 2, pp. 625–630, 2006.
- [42] H. Fritze, "High-temperature piezoelectric crystals and devices," *Journal of electroceramics*, vol. 26, no. 1–4, pp. 122–161, 2011.
- [43] S. Zhang and F. Yu, "Piezoelectric materials for high temperature sensors," *Journal of the American Ceramic Society*, vol. 94, no. 10, pp. 3153–3170, 2011.
- [44] J. Bennett, T. R. Shrout, S. J. Zhang, P. Mandal, A. J. Bell, T. J. Stevenson, and T. P. Comyn, "Temperature dependence of the intrinsic and extrinsic contributions in BiFeO<sub>3</sub>-(K<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub>-PbTiO<sub>3</sub> piezoelectric ceramics," *Journal of Applied Physics*, vol. 116, no. 9, 2014.
- [45] P. M. Weaver, C. Baldauf, T. J. Stevenson, T. Quast, G. Bartl, T. Schmitz-Kempen, M. . Cain, and M. Stewart, "High Temperature Piezoelectric Actuators - Materials and Measurement," in *Proc. Actuator 2014, Bremen, Germany, 2014*, pp. 60–63.
- [46] T. Stevenson, T. Quast, G. Bartl, T. Schmitz-Kempen, and P. Weaver, "Surface mapping of field-induced piezoelectric strain at elevated temperature employing full-field interferometry," *Ultrasonics, Ferroelectrics, and Frequency Control, IEEE Transactions on*, vol. 62, no. 1, pp. 88–96, 2015.
- [47] T. Stevenson, D. Martin, P. Cowin, A. Blumfield, A. Bell, T. Comyn, and P. Weaver, "Piezoelectric materials for high temperature transducers and actuators," *The Journal of Materials Science: Materials in Electronics*, vol. (in press), 2015.
- [48] T. Comyn, T. Stevenson, and A. Bell, "Piezoelectric properties of BiFeO<sub>3</sub>-PbTiO<sub>3</sub> ceramics," *Journal de Physique IV (Proceedings)*, vol. 128, pp. 13–17, 2005.
- [49] J. Bennett, A. Bell, T. Stevenson, and T. Comyn, "Tailoring the structure and piezoelectric properties of BiFeO<sub>3</sub>-(K<sub>0.5</sub>Bi<sub>0.5</sub>)TiO<sub>3</sub>-PbTiO<sub>3</sub> ceramics for high temperature applications," *Applied Physics Letters*, vol. 103, no. 15, p. 152901, 2013.

- [50] W. Wersing, "Small signal resonance methods," *Piezoelectricity: Evolution and Future of a Technology* ed. Walter Heywang, Karl Lubitz, and Wolfram Wersing., vol. 114, pp. 423–444, 2008.
- [51] A. Yacoot and M. J. Downs, "The use of x-ray interferometry to investigate the linearity of the NPL differential plane mirror optical interferometer," *Measurement Science and Technology*, vol. 11, no. 8, p. 1126, 2000.
- [52] CEN, EN 821-1:1995 Advanced technical ceramics. Monolithic ceramics. Thermo-physical properties. Determination of thermal expansion. CEN, 1995.
- [53] T. P. Comyn, T. Stevenson, M. Al-Jawad, G. André, A. J. Bell, and R. Cywinski, "Antiferromagnetic order in tetragonal bismuth ferrite–lead titanate," *Journal of Magnetism and Magnetic Materials*, vol. 323, no. 21, pp. 2533–2535, 2011.
- [54] R. Schödel, A. Walkov, M. Zenker, G. Bartl, R. Meeß, D. Hagedorn, C. Gaiser, G. Thummes, and S. Heltzel, "A new Ultra Precision Interferometer for absolute length measurements down to cryogenic temperatures," *Measurement Science and Technology*, vol. 23, no. 9, p. 094004, 2012.