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1 Executive Summary

Introduction

This project set out to develop new Metrology capability to provide accurate and traceable characterisation of new piezo-electric and electrocaloric materials for both high temperature industrial and solid-state cooling applications. These materials promise energy savings and greater industrial efficiency, but their characterisation is difficult, especially at high temperature. This project has resulted in new materials being developed that are now entering the market, improved measurement techniques, and improved commercial materials characterisation equipment.

The Problem

High temperature Piezo-ceramic materials are needed to enable a new class of sensors and actuators to be developed that operate at higher temperatures, enabling sensing and non-destructive testing in high temperature industrial environments that will lead to greater process efficiency and plant lifetime. Existing commercial equipment and methods are limited in the maximum temperature of operation

There are no robust metrological measurements or methods for the traceable characterisation of potential materials for solid-state refrigeration. Traceable measurements and improved metrics of material performance will provide better material understanding, potentially leading to greater efficiency and reliability in cooling applications.

The Solution

The solution involved developing a number of new measurement capabilities. These provided complementary information and enabled greater confidence to be gained in the measurements.

For the piezoceramics the systems used interfrometric and electromechanical resonance methods to determine the sample piezoelectric response with temperature and applied electric field.

For the electrocalorics a completely new thermographic measurement facility was developed and characterised, this involved upgrading complementary capability at other NMI partners to provide new data on the materials involved.

A number of new computer models were needed to help develop the capability and to better interpret the materials measurement results.

To underpin this work, new piezoceramic and electrocaloric materials were developed by two REG partners (ULE, CU).

Impact

The project developed new metrology capabilities at several NMI partners for high temperature piezoelectric sample measurement. Good agreement was demonstrated between the NMIs and the industrial partner. As part of this project aixACCT Systems have developed several new sample mounts to add to their existing industry leading Piezo-ceramic measuring instruments, which have been validated by measurements at the NMI partners. These instruments enable accurate measurement of piezoelectric properties over a much wider temperature range than was available previously, making it easier and cheaper to develop new devices using high temperature piezoceramics, and therefore helping their uptake into industry and academia.

The enhanced Thermophysical measurement facilities will enable end users to have traceable measurements of their materials, enabling better design and performance modelling for their application.

The new high temperature piezoceramic materials produced in the project are being actively developed further by Ionix Advanced Technology (a spin-out company of the University of Leeds who employed the REG researcher after the project) and are being developed into commercial products for sensing in harsh industrial environments. This will enable higher operating temperatures and hence higher efficiency operation in industrial applications. The company has grown rapidly since the project finished and further growth to address industrial demand is planned.

The combination of Ionix work with aixACCT instrumentation means that there are no longer significant barriers to the commercial exploitation of high temperature piezoelectic materials.

This electrocaloric measurement capability will support the further development of these materials for potential cooling applications. The Electrocaloric figure of merit proposed will help researchers better compare between different materials for their potential in solid-state cooling applications.

2 Project context, rationale and objectives

The efficiency of many industrial processes is determined by the operating temperature. In many applications there is a need to provide sensing and actuation at elevated temperatures in order to monitor and control the processes, including non-destructive sensing. Improvements in these functions will enable reductions in energy consumption and improvements in efficiency and reliability in automotive, energy, process, electronics and medical industries.

One important class of materials that are used at Ferroelectric materials that can couple electrical, strain and temperature responses, making them important for sensing and actuation applications. A recent advance also makes them potentially very useful for all solid state cooling applications. Industrial applications of these materials is held back by several issues, one is high quality and traceable measurements to enable benchmarking of the materials. The existing measurement standards (where available) are only applicable to room temperatures and thus need to be extended to higher temperatures.

These applications exploit the actuation, sensing and cooling functionality of ferroelectric materials which result from strong coupling between electrical, thermal and mechanical properties. Degradation of materials properties at high temperature means that these applications are currently limited to operating temperatures below 200 °C. New materials technologies are emerging to meet this need for high temperature operation, but are not currently supported by a metrological framework for traceable measurement of the coupling at high temperatures.

Need: Reliable, accurate and traceable measurement of electro-thermo-mechanical coupling at high temperatures is essential to provide the data required for the development of new materials technology, effective design of new devices, reliability in characterisation and testing, and to ensure quality in manufacture and reliability in service. This requires a robust measurement infrastructure that is traceable to national and international standards for SI units, and providing measurements under industrially relevant harsh environments (which do not currently exist.) This need is recognised by the collaborators from European aerospace, automotive, power, oil & gas and medical sectors, and a manufacturer of test and measurement equipment participating as an unfunded JRP-Partner.

Aim: This project aimed to develop the metrological infrastructure and facilities within Europe for the traceable metrology of coupling between thermal, mechanical and electrical properties in new materials technologies at high temperatures and high electric fields, enabling their wider commercial exploitation.

How: The project developed new techniques and facilities for the traceable measurement of electro-mechanical, thermoelastic and electrothermal coupling at high temperature. Temperature and thermophysical properties are central to this, so their measurement is also required. These activities are integrated through new models of the coupling and the measurement process.

The project had the following objectives:

1. To develop facilities for the traceable measurement of electromechanical and thermoelastic coupling at high temperatures (up to 1000 ºC) and under high electric fields (up to 5kV/mm) using new high temperature interferometry and new high temperature resonance methods.
2. To develop novel facilities for the traceable measurement of electrothermal coupling and electrocaloric figure of merit in bulk and thin films under high electric fields at temperatures up to 250 ºC.
3. For the first time, to extend high accuracy traceable full-field interferometry of electromechanical and thermoelastic coupling to high temperature applications up to 200 ºC.
4. To develop traceable measurement of temperature and thermophysical properties up to 1000 ºC.
5. To develop new models of the metrological linkages between thermo-electro-mechanical coupling in materials and the measurement protocols developed in the previous objectives and performance in devices.
6. To provide state of the art new materials technologies and apply the metrology developed in this project to the development of new high temperature materials.

Objective 2 and part of 4 were concentrated on electrocaloric materials, and the others were primarily on piezoelectric materials.

3 Research results

Develop facilities for the traceable measurement of electromechanical and thermoelastic coupling at high electric fields up to 1000 °C using new high temperature interferometry and new high temperature resonance methods.

At the start of the project a webinar workshop was organised along with a questionnaire that was designed to capture the measurement needs for the materials that could be developed in the project. This workshop helped to highlight the number of different applications and different material property needs, and also helped to build awareness of the project and stakeholder contacts.

NPL and PTB shared expertise in the development of suitable sample specification that could be measured in the two metrological interferometric instruments and identified a company that was able to deliver the very exacting specifications required. Test samples of a commercially available piezoceramic were sourced to enable the instruments to be commissioned and tested while REG(ULE) developed the new composition of higher temperature materials.

Interferometer

An investigation of high precision interferometer methods was undertaken and a modified Jamin design chosen as it uses a common path design to minimise path length differences that occur in parts of the system other than the sample being measured. As the system needs to operate at a large temperature range there are going to be unavoidable thermal expansions and distortions. It was decided that the interferometer needed to operate in vacuum as no suitable data was available for elevated temperature air refractive index and any air convection would severely affect the interferometer operation. PTB's expertise in precision interferometry was invaluable in the design phase. The furnace features a large uniform temperature region in the centre and a large sapphire window in the top for the interferometer and non-contact temperature measurements. Electrical excitation is provided via vacuum feed-through and a 20 kV voltage amplifier.

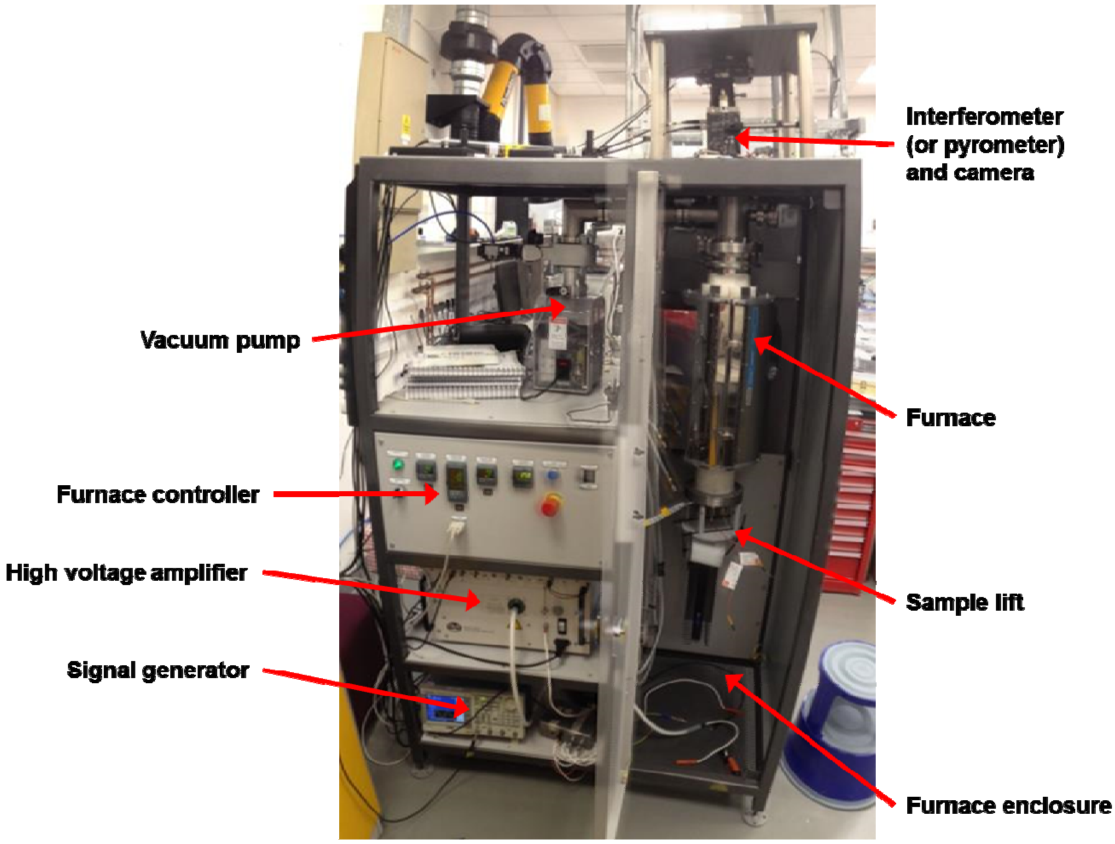

Figure 1 Custom vacuum furnace and interferometer at NPL

A custom vertical three-zone vacuum furnace (**Error! Reference source not found.**) was designed in collaboration with Carbolite, a UK manufacturer of industrial and custom furnaces. Slight delays in agreeing the design and placing the order lead to significant delays due to Carbolite winning a separate large complex bid that was to be delivered before the METCO furnace. The sample temperature was measured close to the sample with a calibrated thermocouple, temperature differences were determined using a dummy sample (Figure 2). High purity Alumina parts were used to ensure the highest degree of electrical insulation between the high voltage excitation and the rest of the experiment, the furnace was carefully earthed in case of accidental electrical breakdown.

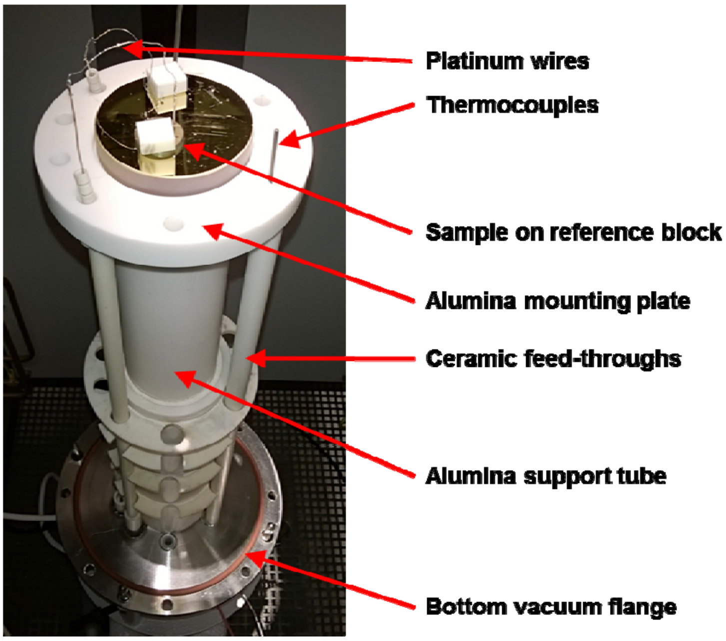

Figure 2 Sample mounting inside the vacuum furnace

Similarly to the PTB design the sample to be measured needs to be mounted in contact with a flat reference surface and the distance between this surface and the top of the sample measured. Unlike the PTB system this design can only measure relative difference changes (expansions), not the absolute length.

In order to be measured the sample needs to be “electroded”, that is coated on both main faces with a coating that is very thin (so its expansion is not measured), is highly reflective (to enable it to be measured) and to be electrically conductive (so that the electrical isolation can be applied to the sample). At near ambient temperatures this is usually done with a vacuum deposited gold coating with a titanium adhesion layer. Higher temperature alternatives such as Platinum-Rhodium were discovered, but they were too expensive to test. Some tests on a Tantalum-Platinum coating were done but they did not offer much improvement in performance and they did not adhere well to the crystal samples that could be measured at the higher temperatures.

Unlike the PTB interferometer system, a commercial 10 mm thick quartz optical flat was used for the reference surface due their commercial availability and high optical performance.

Custom software was written to control the furnace and measurement cycles including sample excitation. A fast electrical sampler was used to continually keep track of the interferometer phase (as it only measures relative changes in displacement) (Figure 3) which is quite noisy due to thermal and mechanical effects. Due to the slow rate of change of temperature possible with the furnace measurements were made at intervals during a very slow temperature ramp.

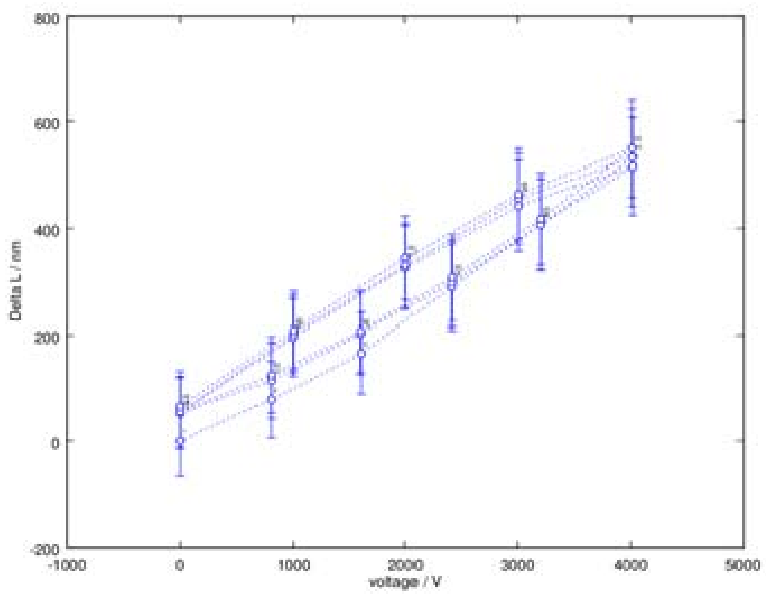

Figure 3 Typical unipolar excitation measurement using the NPL interferometer

A survey of pyrometers was made and a suitable unit purchased. The original plan was to measure the temperature of the resonance samples in non-contact, but as this was not possible the decision was made to use it to measure the sample temperature in the interferometer, especially to look for "self-heating" which can occur when samples are excited with large voltage high frequency signals. This self-heating can lead to failure of the sample. For this the sample needs to be coated in a suitable high temperature capable high emissivity paint to minimise temperature measurement errors, evaluation of suitable paints was undertaken by LNE. Several coats were needed to ensure the paint performed as required.

The Pyrometer was calibrated against previously calibrated thermocouples mounted close to the sample, this removed the requirement for performing transmission and size of source corrections. An uncertainty budget was constructed with input from MIKES.

The self-heating experiments (Figure 4) showed that as the sample temperature increased, the amount of self-heating increased significantly, this was due to internal resistive losses as the material got closer to its Curie temperature. The uncertainty in a 40 °C temperature rise was estimated as 1.5 °C (to 95 % confidence).

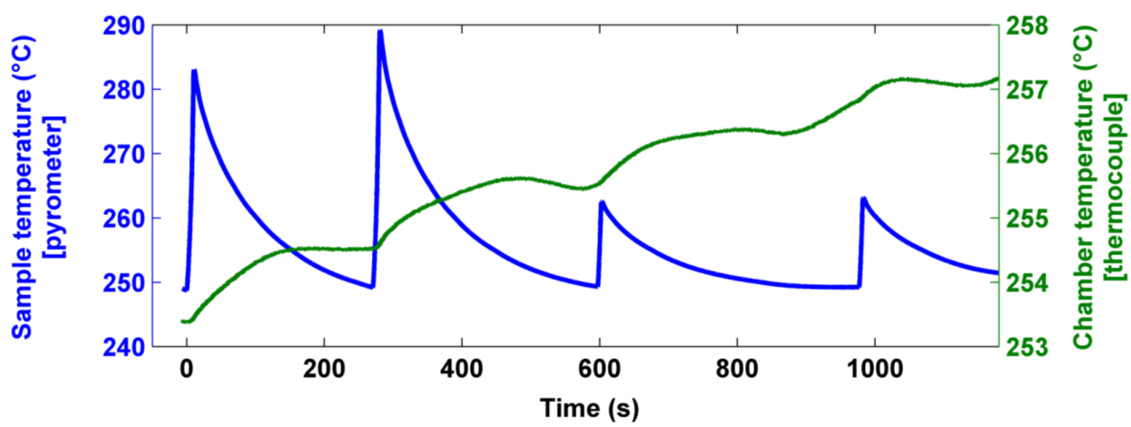

Figure 4 Self heating of a test sample

In industrial operation these materials maybe mounted differently, which may affect the heat flow and effect of self-heating, the system developed could easily be modified to enable measurements on industrial trial samples.

It was initially planned that both Quartz and Gallium Orthophosphate crystal could be used and demonstrated as potential high temperature reference materials. Electroding of these materials was found to be hard (similarly to the ceramic samples) and also there was difficulty in getting measurements of them.

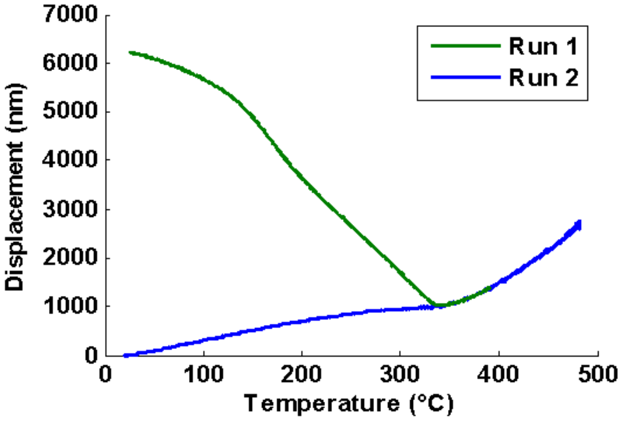

Figure 5 Thermal expansion of PZT at first and second heating

The system was able to also measure the thermal expansion of the samples, Figure 5 shows an example of this measurement. The negative expansion on Run1 was due to the poled piezoelectric nature of the sample, which is lost when the sample was heated beyond the Curie temperature (around 350°C in this case) and then Run2 measured the un-poled thermal expansion of the bulk ceramic.

Electromechanical resonance measurements

The second system developed by NPL was to accurately measure the piezoelectric performance using a "resonance method", whereby a specially shaped ceramic sample is electrically excited, the resonant frequency, sample size and density enable the piezoelectric properties to be determined. The samples and measurements will follow the existing **EN 50324-2:2002** *"Piezoelectric properties of ceramic materials and components —Part 2*: *Methods of measurement —Low power*" standard (though it is only valid for measurements made at room temperature). This standard uses a number of specially shaped ceramic samples that are measured and the ceramic piezo parameters are then calculated using the standard formulae.

The work identified a number of issues (including increasing electrical losses) when measuring samples at elevated temperatures and through their Curie temperatures (where they cease being Piezoelectric).

A commercial Thermomechanical Analyser system was bought and modified to enable the electrical excitation and the measurement of the sample response using a microwave Impedance analyser which was suitably calibrated and experiments were carried out to quantify temperature induced measurement errors in the measurement set-up. Care was required to hold the samples so that the clamping force did not affect the measurements.

Work was required to accurately characterise and correct the sample temperature measurement in the instrument due to temperature gradients present. This used samples of pure metals with known melting points, a temperature uncertainty of ±5 °C was achieved. The original plan called for a non-contact pyrometer to measure the sample temperature, this was found to be impractical due to the small size of the samples and the need for them to be coated in a reflective and electrically conductive coating, which makes pyrometric temperature determination inaccurate. The pyrometer was then used to measure the self-heating in ceramic samples in the interferometer.

Figure 6 shows an example of the measurements made with increasing temperature, showing the shifts in the electro-mechanical resonances and their disappearance above the Curie temperature (400 °C in this case). A full uncertainty budget was created, taking into account all the different effects and repeatability, an uncertainty in the d_{33} parameter of 294 pm/V of 7.2 pm/V (95 % confidence) was derived for one sample at 347 °C, the largest contribution being from the measurement of the mass of the sample.

Work as carried out comparing the standard analysis with that of a commercial program "PRAP", which performs mathematical fits to the measurement data to derive the required parameters and does not make any assumptions on the temperature variation of some of the sample properties (as the Standard method does). Good agreement was found in some cases, but differences were found (by fitting the actual data PRAP can obtain better estimates from poor data, especially at high temperatures when the samples exhibit increasing electrical loss. Unfortunately derivation of uncertainties for PRAP was not possible due to the proprietary nature of the software, this is something that should be done in future. To address this a custom Monte Carlo method was developed that showed good agreement to PRAP at lower temperatures, but which needed more work to fully account for all the possible sources of error.

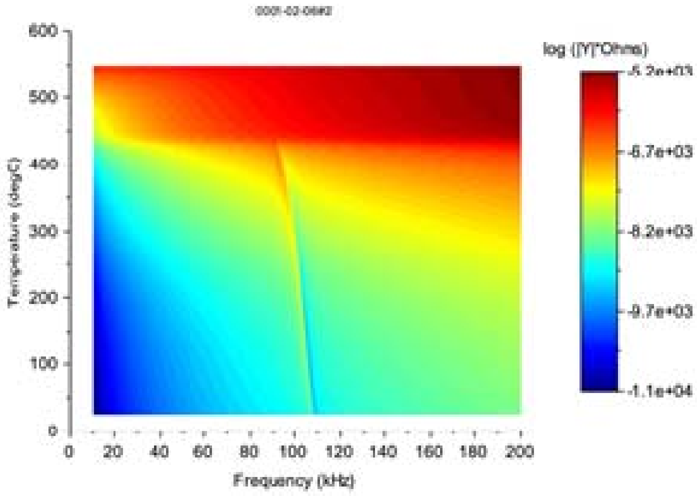

Figure 6 Temperature dependence of the piezoelectric resonance spectra for KBT-BFPT sample measured using the NPL high temperature resonance system.

The system performance was demonstrated by measuring the Piezoelectric response of Gallium Othophosphate and observing its phase transition at 793 °C.

Other commercial system upgrades

AixACCT Systems, the commercial partner of this project developed (with help from a short duration REG) a number of new sample mounts that can be used with their existing piezo material measuring systems (both single and dual beam interferometer), this enables industrial and academic end-users to buy equipment to do the measurements in their own premises, but with confidence in the measurements they make. The new single beam sample mount (Figure 7) enables measurements up to 800 °C and the dual beam system up to 600 °C for thin film samples.

Temperature accuracy using a specially developed dummy sample with embedded thermocouple and the results were fed into a measurement uncertainty budget that also included contributions from the electrical system (detection and excitation), dimensional drifts and repeatability.

They evaluated the performance of the system using a range of samples including Quartz which has a well understood phase transition at 570°C.

Figure 7 High temperature sample mount upgrade for aixACCT single-beam interferometer measurement system.

Inter-Comparisons

A detailed comparison protocol was written with input from all the project partners, with special care taken to keep track of the temperature and electrical excitation that each sample had undergone as these can lead to subtle changes in the samples which will invalidate any instrument comparison. Example plots can be seen in Figure 8 and Figure 9,

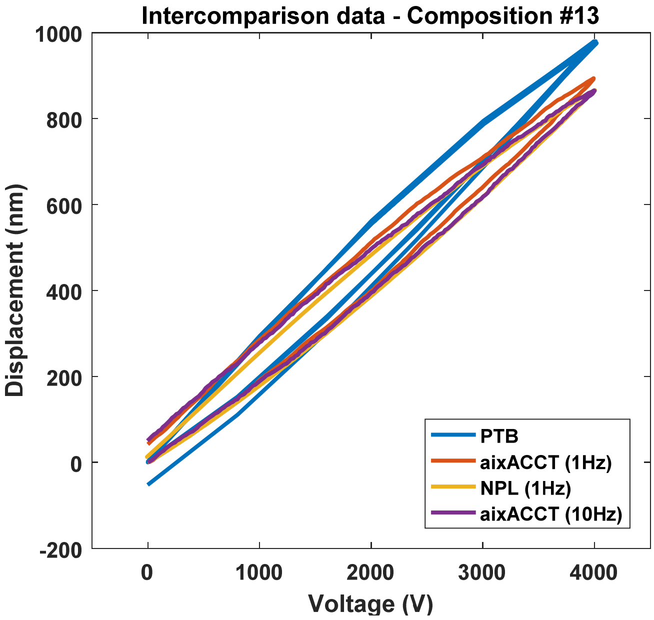

Figure 8 Comparison of interferometric measurements (PTB deviation likely to be due to operating <<1Hz Figure 9)

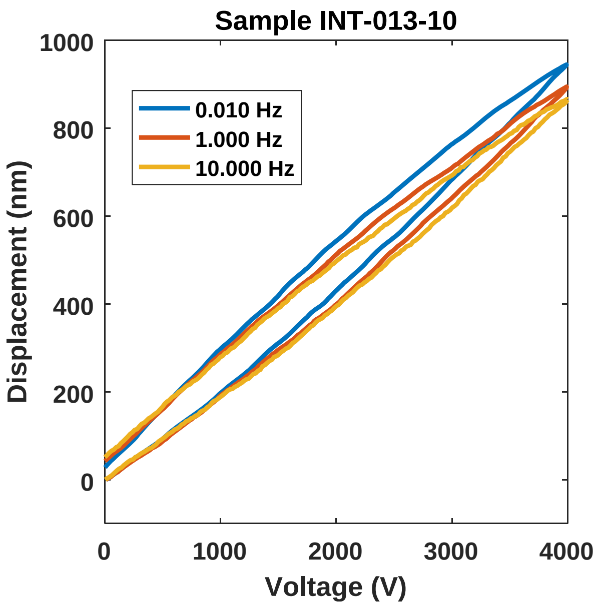

Figure 9 Measurement frequency effect on the measured sample displacement

This work lead to a publication "High temperature measurement and characterisation of piezoelectric properties", J.Mat.Sci. Materials in Electronics, Weaver et al, 10.1007/s10854-015-3285-8.

Develop novel facilities for the traceable measurement of electrothermal coupling and electrocaloric figure of merit in bulk and thin films under high electric fields at temperatures up to 250 ºC.

Electrocaloric coupling is the response of a ferroelectric material where an induced electric field change creates a temperature change in the material. This effect could be exploited in developing novel solid state coolers for industrial and IT applications. The field is quite new and many papers are being published, many of them derive the Electrocaloric performance from other measurements, where assumptions have been made, which can lead to the significant differences between nominally identical materials.

The project developed a facility that could be used to provide traceable assessment of the direct and adiabatic Electrocaloric response of different materials and also develop better metrics to enable objective comparison of materials so that their suitability for industrial use could be more easily determined. Much of the research focusses on thin-film (<1 micron thick) films of material which can exhibit greater electrocaloric response, whereas others make measurements on bulk (mm scale) samples, the measurement capability was designed to address both of these options.

Given the tiny amount of material in the thin-film sample, environmental heat-losses can dominate and so careful sample design was needed for the experiments. The Cranfield REG developed a number of test film samples where the supporting substrate had been etched away to reduce conductive losses. Designs using a resistive thermometer, a thin-film thermocouple deposited on top of the film and for non-contact thermometer measurement were created and produced (Figure 10). The extra material and potential for electrical interference and stray heating meant that a thermal camera was also used for measuring the sample temperature rise.

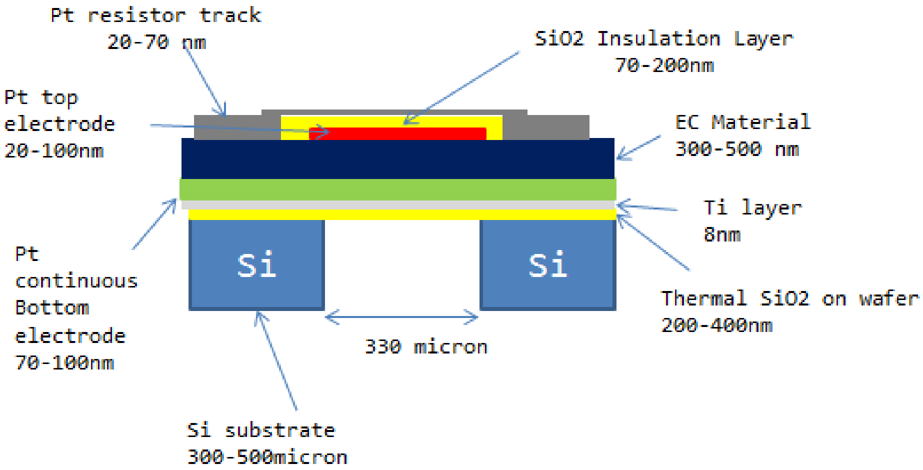

Figure 10 Cross section of resistive temperature sensor on a thin-film sample**.**

A high resolution, high speed thermal camera (Infratec ImageIR 8320) was purchased that could image the thin-film samples (typically <400 µm across), the temperature and effect of sample emissivity needed to be carefully calibrated to enable the small temperature changes to be accurately measured.

NPL designed and constructed an Electrocaloric test facility that enabled the measurement of samples (both thin-film and bulk) at temperatures from ambient up to 200 °C in both air and vacuum environment, with the ability apply up to 10 kV to the sample (fields up to 1500 kV/cm for thin-film samples). A large sapphire window was needed on the top of the sample chamber to enable measurement of the samples with a thermal camera. Depending on the size of sample the timescale for the Electrocaloric temperature response could be from sub-second to a few minutes. The facility also allowed the measurement of ferroelectric P-E loops, which provides additional useful in formation in understanding the samples. Finally the system will provide measurement of the heat capacity and thermal conductivity of the samples, which will compared to measurements made at LNE, thus validating the new facility.

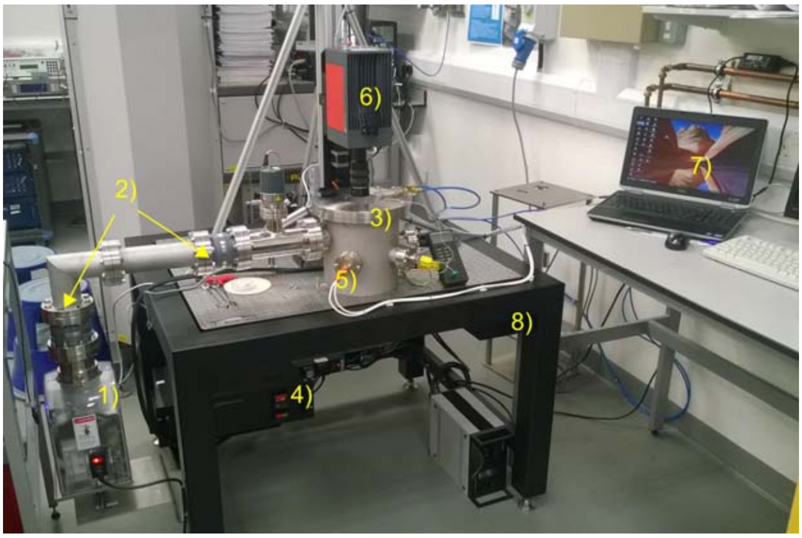

Figure 11 NPL Electrocaloric test facility with vacuum chamber and thermal camera

The sample heater enabled the sample chamber to be stably controlled up to 250±1 °C. There were some initial issues with vacuum pump vibrations affecting the thermal camera (which has a small field of view as the samples are typically 0.5 mm across, these were resolved by using vibration isolation bellows in the vacuum line and a vibration isolation table for the sample chamber and camera (Figure 11). The thermal camera was calibrated for sensitivity, drift, uniformity against a traceable reference black-body source and its size of source error derived. In testing, to eliminate errors from sample emissivity, measurements of carbon-nanotube forest samples (reflectivity <0.05 %) were made.

A range of test samples with a range of compositions were obtained from the project stakeholders.

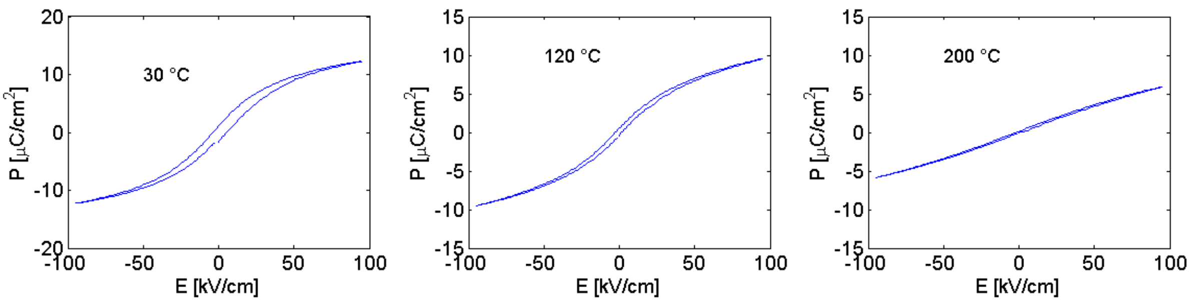

Figure 12 Representative P-E loops acquired in the X7R MLCC at 1Hz (PE loops taken upon rising temperature)

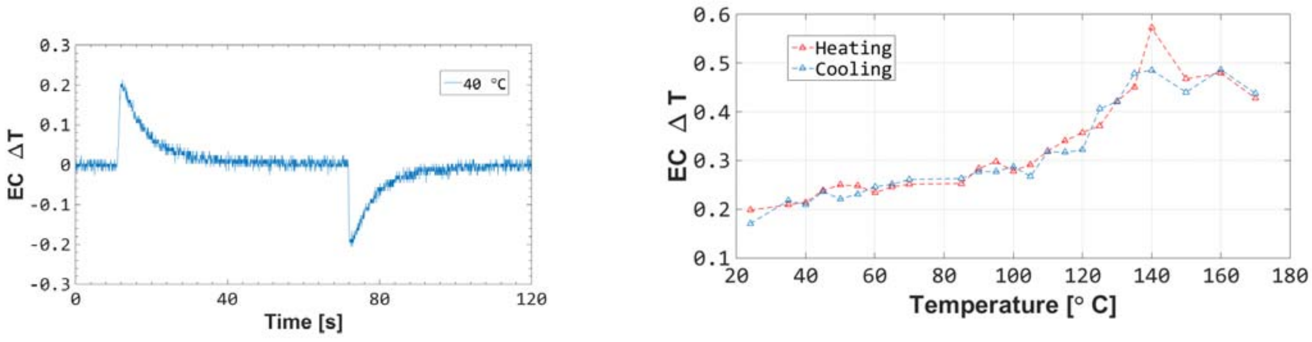

Figure 13 Directly measured EC effect at the cross-section of the X7R capacitor, for the 90 kV/cm with the rising time corresponding to 1 Hz (left)) time-resolved at the 40 °C plot and (right)) temperature-resolved for the heating peak (exothermic) and cooling peak (endothermic)

The electrocaloric response of the bulk samples was successfully measured (Figure 12, Figure 13), but the thin-film samples did not yield good results and suffered electrical breakdown, probably due to issues in the electrocaloric ceramic thin-film quality. It was not possible to source any suitable replacement samples.

A full uncertainty budget was produced that included sample geometry measurements, electrical excitation, stray light and emissivity, instrument calibration and repeatability was constructed.

NPL hosted a meeting attended by a number of academic experts on Electrocaloric materials to discuss the options for developing a "Figure of Merit" that could then be used to compare different Electrocaloric materials in a reliable way, enabling people to assess their suitability for use in solid state cooling applications. The outcome were two figure of merits where proposed material (Eq 1) and device–like (Eq 2):

$$FoM_{EC} = Q \cdot \kappa \cdot \eta \quad \text{in [J W m}^{-1}\text{ K}^{-1}] \qquad \text{Eq. 1}$$

$$\mathrm{FoM_{Device}} = \mathrm{COP} \cdot \mathrm{RC} \cdot \frac{F_o}{\tau_c} = \frac{c\,\Delta T_{EC}{}^2 \delta T \lambda}{\varepsilon\varepsilon_0\,E^2 \tan\delta} \cdot \frac{a}{T \cdot E^2 \cdot d^2} \quad \text{in [W]} \qquad \text{Eq. 2}$$

Where for the Eq 1 Q is electrocaloric heat change, κ thermal conductivity of EC material, η EC efficiency. For eq. 2 the FoM is composed of the coefficient of performance (*COP*) refrigerant capacity *RC* and the furrier number *Fo* divided by τ_c time constant of thermal cycle and where the c is the volumetric heat capacity, ΔT_{EC} EC temperature change, λ thermal diffusivity, E electric field, d a characteristic device length, $\varepsilon\varepsilon_0$ and $tan\delta$ relative permittivity and the loss.

This work has led to Maciej Rocosz undertaking a joint PhD with Imperial College to take this work further. Joint work at LNE to measure the thermal diffusivity under electric field, also round robin testing with Imperial College to verify their measurements of state of the art samples.

For the first time, extend high accuracy traceable full-field interferometry of electromechanical and thermoelastic coupling to high temperature applications up to 200 ºC

PTB had previously extended the temperature range of their reference gauge block Ultra Precision Interferometer from operating only at ambient to being able to operate down to liquid nitrogen temperatures. The interferometer uses three laser wavelengths and a phase stepping method to measure the absolute length difference between a flat reference plane and the top surface of a sample placed on top of if. For accurate measurement the samples must have top and bottom surfaces that are very parallel to each other and have an extreme degree of flatness. The samples are "wrung" to the reference flat (to eliminate any air gaps that would cause errors in the length measurement). The interferometer uses three different wavelength frequency stabilised lasers and a "phase stepping" technique, measuring the interference pattern across its field of view and so can produce accurate height maps of the samples that are being measured, unlike the NPL and aixACCT systems that could only make point measurements.

The NPL interferometer had less demanding requirements, but making all the samples to the same specification (30 nm flatness, <4arc second parallelism, roughness <5 nm) enabled both systems to check the same samples, needed to ensure the comparability of the systems. Significant effort was required to find a company that was able and willing to polish piezoceramic samples to the tolerances required, the only company found was Kolb & Baumann (KoBa) in Germany.

PTB designed a new insulated heater stage (Figure 15) to heat the sample up to 200 °C and enable up to 2 kV to be applied to the sample and that could be mounted inside their existing interferometer vacuum vessel (Figure 14) and heat the sample and reference plate. The reference block was made from Aluminium Nitride which is electrically insulating, but has good thermal conductivity to minimise temperature gradients and ensure that the reference Platinum thermometers mounted in it gave an accurate measurement of the sample temperature. Weighted probes were used to maintain electrical contact to the top surface of the sample as it was heated up. The entire sample environment had to be well thermally shielded to prevent radiative heating of the rest of the interferometer which would affect the instrument performance.

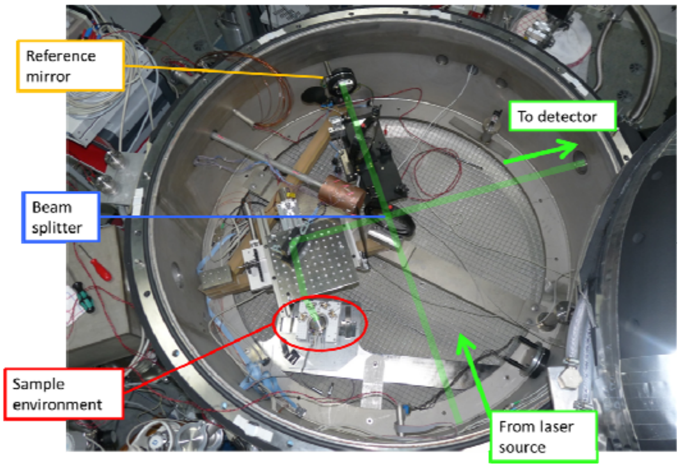

Figure 14 New sample enclosure inside the PTB interferometer chamber.

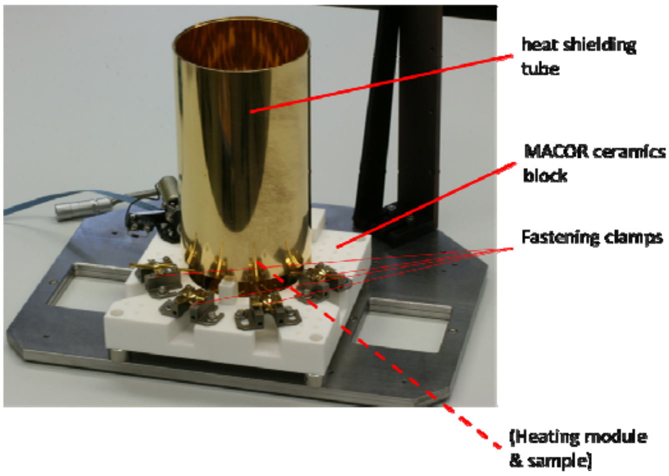

Figure 15 PTB Interferometer sample mount (normally surrounded by a heat shield).

During testing vibrations were detected that prevented accurate measurements, a more robust sample stage mount was built which eliminated these. The Platinum thermometer also got damaged and required a recalibration, which led to a slight delay in the work. Measurements at each temperature took much longer than for the NPL interferometer, so the measurements needed to be taken at stable temperature steps

The sample stage demonstrated very good temperature stability, with changes of less than 40mK over two hours. As the interferometer measurements take many minutes to acquire it is important that the sample does not expand during the measurement. Tests were made looking at the electrically induced displacement of PZT at several temperatures (Figure 16). A full uncertainty budget including terms from the interferometer, sample stage and electrical excitation system were constructed with a typical absolute length error on the order of 66nm.

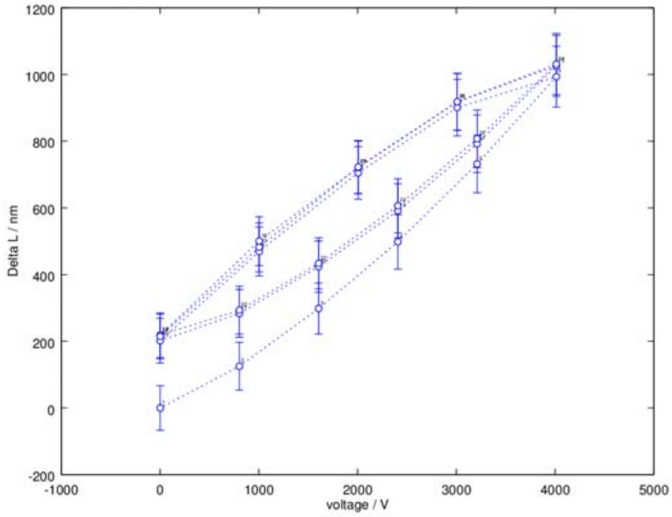

Figure 16 Unipolar loops for INT-011-12 at 101°C with side B facing up

As the interferometer is able to measure the spatial variation of the sample height it was able to detect sample bowing that was caused either during the electrical excitation or the heating cycle (Figure 17). The deformation caused problems for the interferometers to make accurate measurements as the samples were then out of specification. This limited the comparison measurements to a lower temperatures, as the warping would result in a change of sample performance, preventing an accurate comparison of measurement systems.

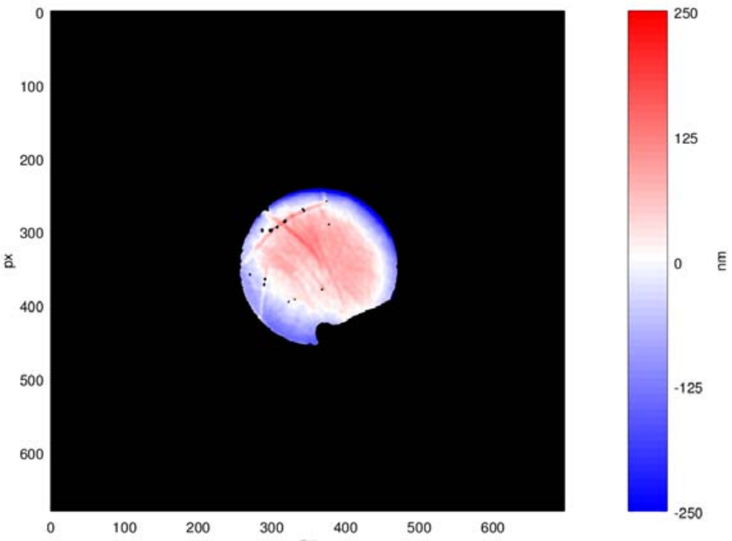

Figure 17 Interferomgram showing 300nm sample bowing

Thermal expansion measurements of the samples were undertaken and compared to NPL.

As the piezoceramic response is very temperature, frequency and voltage dependent, great care was required to find similar conditions to enable a meaningful comparison of the measurement systems (Figure 18).

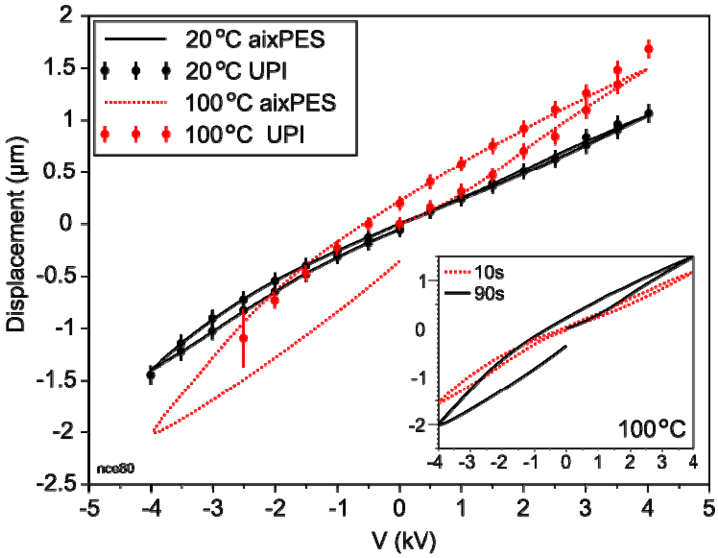

Figure 18 Comparison of PTB UPI system and aixACCT commerical piezo-measurement system

This work resulted in a publication "Surface mapping of field induced piezoelectric strain at elevated temperatures employing full-field interferometry", Stevenson et al, IEEE TUFFC Special Transactions, 62, 88-96 (2015).

Develop traceable measurement of temperature and thermophysical properties up to 1000 ºC

This activity was required to provide data of the material properties to help with modelling activities and the accurate measurement of the non-contact temperature measurements that were to be undertaken in the other work packages, the capability for making the measurements did not exist and needed to be developed in the project. The work was undertaken by LNE and MIKES, with some sample production from REG ULE and materials expertise from NPL.

The sample geometries needed to fit into the different existing Thermophysical measurement instruments of the partners was undertaken. One issue identified was the effect of the polling state of the ceramic and the ability to apply an electric field to the sample during the tests. Suitable test samples were produced by the Leeds REG.

Emissivity at high temperatures

MIKES (along with REG(ULE) on secondment) undertook measurements of the candidate high temperature Piezoceramic ceramic for spectral emissivity using a furnace, these were needed to enable non-contact thermal measurements of these materials to be undertaken as the emissivity can vary with temperature. A specular emissivity technique was also used as there were some issues with obtaining accurate sample temperatures with thermocouple sensors. Figure 19 shows the results which show the emissivity of the material does not change much with temperature, reducing the potential for measurement errors using non-contact thermometry.

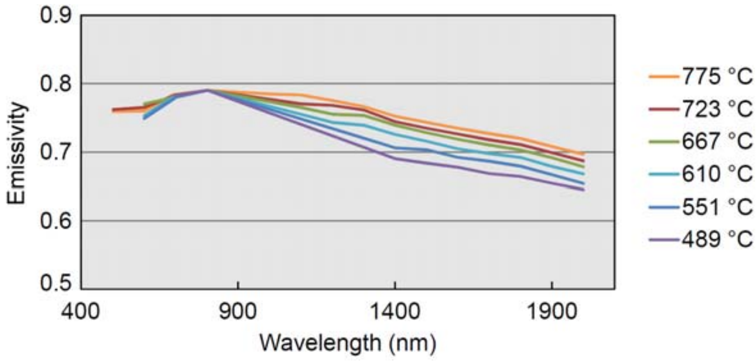

Figure 19 Spectral emissivity of BFPT at high temperatures

This work lead to a publication "Validation of a Blackbody Comparator Based System for Thermocouple Calibration", Ojanen et al, Int. J. Thermophys. , Issue 35, pp. 526-534 (2014)

Hemispherical reflectance

Measured spectral hemispherical reflectance was used to derive the spectral emissivity of the samples up to 800 °C for un-poled Piezoceramic samples (this was needed for the non-contact temperature measurements), as such no modifications to the measurement instrument were required, though custom samples were needed to be produced. Changes were seen in the near-infrared (Figure 20), though this will not affect the non-contact thermography used in the interferometric system.

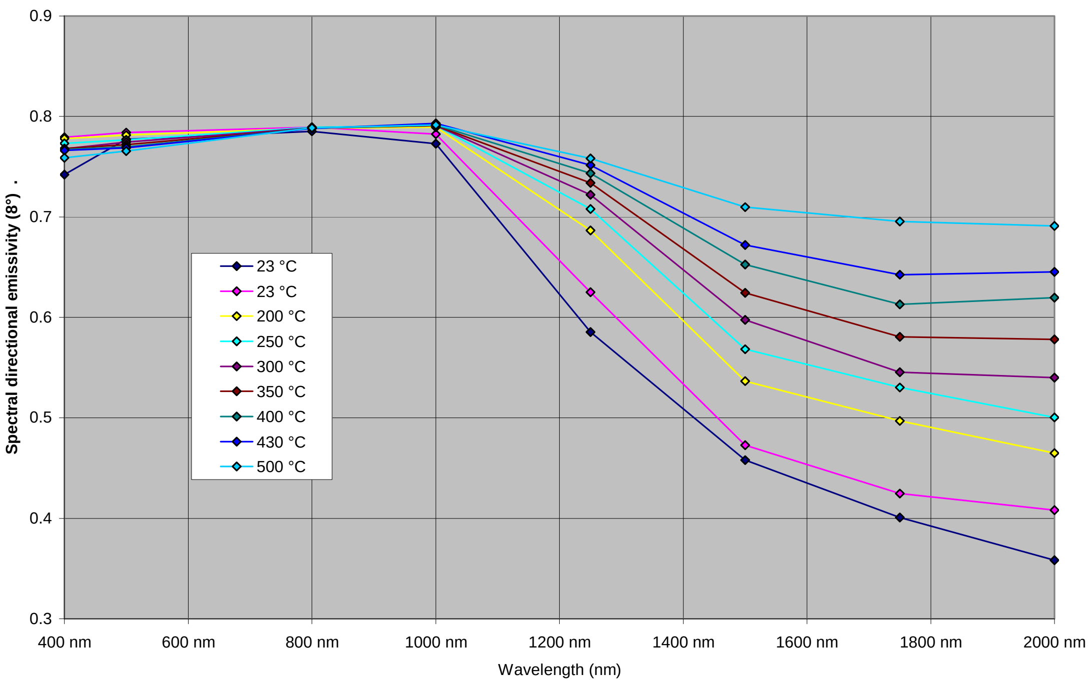

Figure 20 Sample spectral emissivity of un-poled BFPT Piezoceramic with temperature.

Radiative properties of ferroelectric samples to 80 0°C

The spectral emissivity of the samples supplied by REG(ULE) were measured at a range of different applied electrical fields (Figure 21) and no noticeable changes were measured up to 4 kV/mm. This shows that the applied electric field will not cause systematic temperature measurement errors when non-contact thermometers are used to measure these materials.

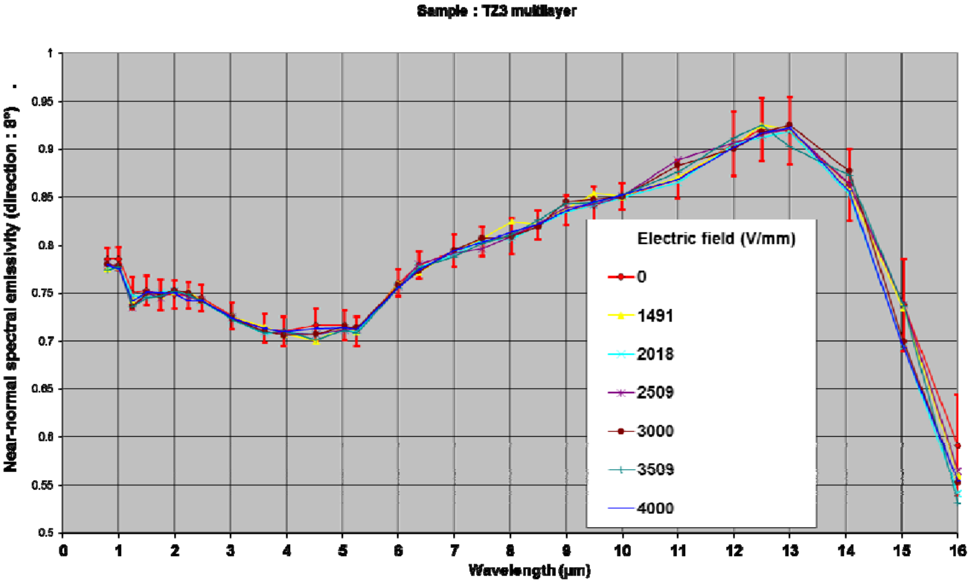

Figure 21 Sample spectral emissivity of un-poled BFPT Piezoceramic with applied electric field

Measurements to enable non-contact measurement for the self-heating

The non-contact thermometric measurement expertise of MIKES was invaluable in helping NPL determine the suitability of potential non-contact thermometers for adding to their measurement system. As was previously mentioned, it was realised that it would not be possible to measure the resonance samples using a non-contact thermometer and so changes to the interferometer furnace needed to be considered and designed. MIKES provided advice on instrument selection, mounting and alignment, data processing and on uncertainty budget calculation. MIKES provided calibration of the instrument and also undertook size of source and temperature sensitivity measurements that were important contributions to be uncertainty budget. LNE provided a survey of the emissivity properties of a number of sample paints (Figure 22) with temperature that were needed to give the sample a high emissivity and hence reduce uncertainty in the temperature measurements.

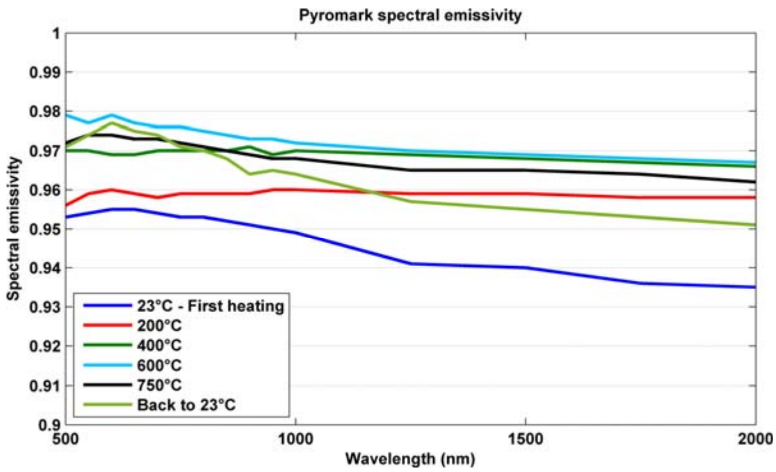

Figure 22: Spectral emissivity of Pyromark 2500 at different temperature conditions

Thermophysical measurements for Ferroelectric materials

To help the modelling and understanding the performance of the Electrocaloric and Piezoceramic materials LNE modified a number of their existing measurement facilities for measuring specific heat, thermal diffusivity and thermal conductivity, with the samples under an applied electric field of up to 2 kV at temperatures up to 800 °C. The measurements needed to be carried out in an inert atmosphere or vacuum to avoid oxidation damage to the samples. Care with electrical insulation was needed as the applied voltages are high and the space available for the modifications small.

The specific heat measurements were carried out using a commercial Differential Scanning Calorimeter (Figure 23), tests were undertaken to ensure that the wires did not affect the heat flow in the instrument and hence cause undesirable measurement errors.

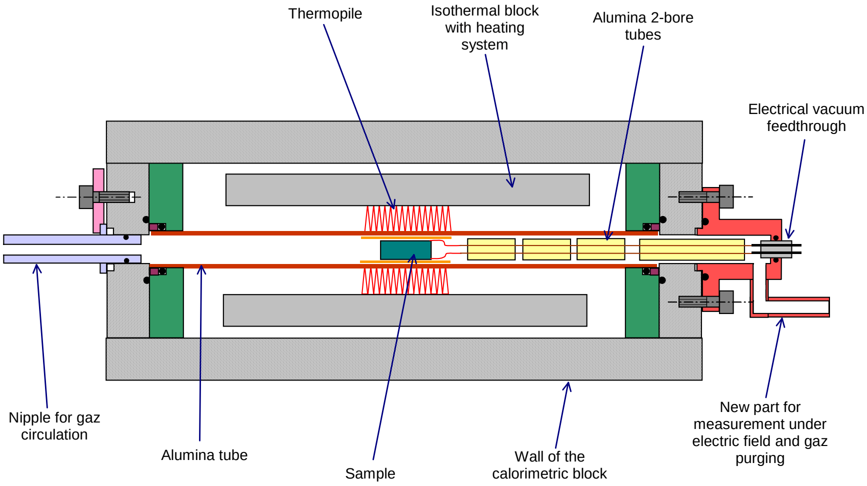

Figure 23 LNE modified DSC sample chamber

The thermal diffusivity measurements were performed on a Laser Flash apparatus where the temperature rise through a sample is measured after it has been heated by a short pulse of laser illumination on the other face. Again modifications to enable sample electrical excitation were needed, but in this case the main faces of the sample cannot be obscured as they are needed for the laser pulse excitation and back side temperature measurement (Figure 24).

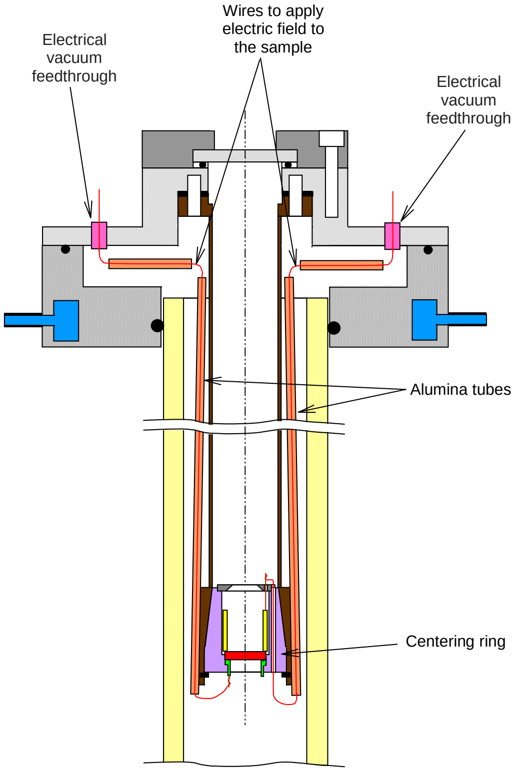

Figure 24 Modification of LNE laser flash sample holder for thermal diffusivity measurements.

For thermal conductivity of thin films (required for the thin-film Electrocaloric samples) the LNE Photo-Thermal Radiometer was modified (Figure 25), this measures the change in temperature from a modulated laser illuminating a heated sample. The modifications involved modifying the heated sample chamber, adding an alumina vacuum feedthrough and designing a ring-and-disc set-up to make electrical connection to the sample but provide enough room for the optical measurement system to measure the sample. The ability to electrically excite samples with this measurement set-up is a unique capability.

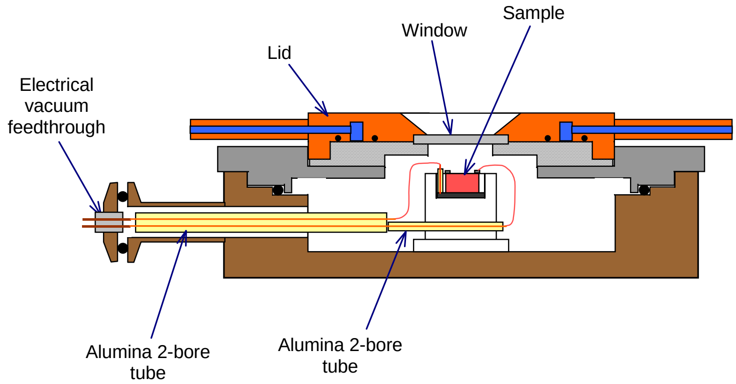

Figure 25 Modified sample stage for LNE Photo-Thermal Radiometer system

A revised uncertainty budget was developed for all three instruments, taking into consideration the modifications that had been made and their effect on the accuracy. The modified facilities were used to measure two different set of samples for their Electrocaloric response, one from a commercial multi-layer capacitor design and other from project Stakeholders. The data obtained was used on the modelling work and resulted in a publication. A member of staff from NPL visited LNE for several weeks to help with the measurements and to exchange measurement and materials expertise.

The data showed that there were no significant changes in the thermal properties of the materials with an electric field applied compared to without a field applied. The laser flash apparatus was used to measure the Electrocaloric temperature change due to a rapidly applied electric field for several of the samples and good agreement was obtained between NPL and LNE demonstrating the confidence in the measurements obtained (Figure 26).

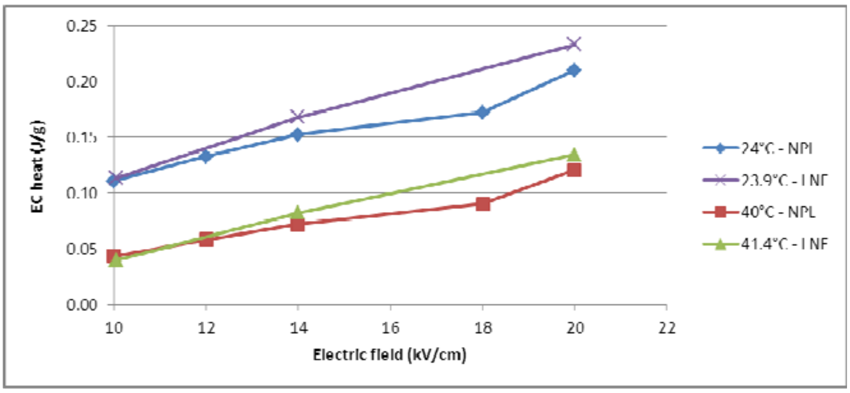

Figure 26 Comparison of measurement of Electrocaloric effect of a Barium Strontium Titanate sample (LNE-NPL Comparison).

Develop new models of the metrological linkages between thermo-electro-mechanical coupling in materials and the measurement protocols developed in the previous objectives and performance in devices.

Modelling was needed to help understand the measurements being made and the underlying coupling of electrical, thermal and mechanical responses. Due to the crystal structure of the materials changes to strain, temperature or electric field will all affect the crystal lattice a non-linear and time dependent way. For use as coolers, the materials will experience heat-flow through them so this needs to be added into the model to obtain a realistic result.

Model 1

The first model was a non-linear one designed to understand the thermodynamic response in Electrocaloric samples where an electrical field change induces a change in sample temperature. This will allow a better understanding of the different coupling effects and features of the material composition. Time and frequency dependence of the coupling, between piezoelectric, electrocaloric and thermal expansion effects, this was needed to better understand the dynamic behaviour of the Electrocaloric materials. Temperature dependent parameters, potential well barrier heights, which reduce as the sample temperature increases. This resulted in a publication “Experimentally validated finite element model of electrocaloric multilayer ceramic structures”, Smith et al, J. Appl. Phys 116, 044511 (2014).

Model 2

A model of the time and frequency dependence of the electrical, strain and thermal effects to understand the time and temperature response of the electrocaloric effect. This built ion previous work by NPL. It predicts that the Electrocaloric effect can be enhanced by application of a controlled electric field, making the materials more useful as coolers over a wider range of ambient temperatures. For thin-film samples where the thermal mass is very small and the thermal response is quick it is important to understand how this will affect the Electrocaloric response of the material as a function of temperature.

Results also predicted the negative thermal expansion seen in the measurements of piezoceramics made by the interferometers.

Model 3

A detailed COMSOL model of a thin film Electrocaloric device such as those measured in the NPL facility, including the substrates, oxide films and electrode coatings was developed, to help predict the potential heat losses (conductive and radiative) that will be encountered, so that the effect on the measurement can be assessed. The temperature distribution of a multilayer capacitor and thin film sample were both modelled, so the predicted time constant and temperature evolution could be determined, this helped with the design and interpretation of the measurements.

Model 4

New models to look at the tip-surface interaction at the nanoscale for Scanning thermal microscopy were developed so that measurements of the fine scale structure of Electrocaloric films can be probed. This is important to understand the cause of variations at the macroscale. Scanning thermal microscopy is complicated by the need to have a complex tip which include heaters to maintain a constant tip temperature. The model uses the realistic tip and surface geometries so that the accurate thermal properties of the material can be determined, unaffected by artefacts caused by the surface topography.

This model was subsequently enhanced to simulate the electrocaloric cooling and subsequent heat flow in the sample that occurred after a change in electrical excitation so that it could be compared to Scanning thermal microscopy images.

Provide state of the art new materials technologies and apply the metrology developed in this project to the development of new high temperature materials.

This work was mainly undertaken by a REG at the University of Leeds (Tim Stevenson). This work was aimed at developing improved ferroelectric materials for use at higher temperatures and that could potentially be used as reference materials for the testing of the measurement systems developed in the project. After a detailed literature search of state of the art high temperature piezoceramics a number of candidate materials were identified for further study; (Bi,La)FeO3-PbTiO3, BiFeO3-PbTiO3 – (K,Bi)TiO3, (Bi,Nb)InO3 – PbTiO3, BiScO3 – PbTiO3. Some of the other materials were discounted as they contained expensive rare earth materials and so they were too costly to produce and subsequently commercialise.

A number of slight compositional variations of the were produced and extensively tested using X-ray crystallography, electron microscopy, electromechanical assessment in order to derive the best candidates for measurement by the project partners. Samples in three compositions suitable for measuring with the interferometers and resonance systems (Figure 27) were then made and electrically poled and sent for polishing to the correct specification and final electrode deposition. A study on the best coating recipe to give highly adherent gold coating.

The results of the Stage1 samples lead to a further set of different improved sample compositions for the Stage2 samples, however it was found that that the changes in composition did not result in the improvements that were expected.

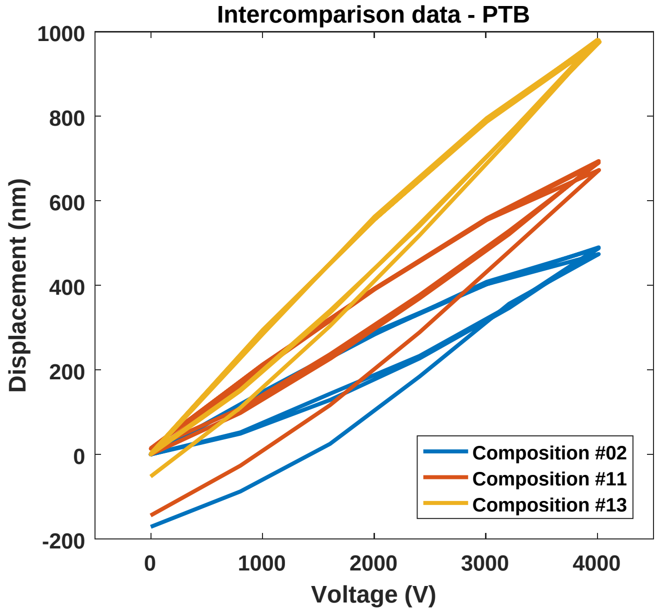

Figure 27 PTB measurements of the three different composition samples from Stage 1

This work resulted in a publication “Piezoelectric materials for high temperature transducers and actuators”, Stevenson et al, J.Mat.Sci. Materials in Electronics, 10.1007/s10854-015-3629-4.

As part of the REG Dr Stevenson undertook a number of training activities at the different project partners:

- MIKES: Spectral emissivity measurements.
- PTB: The design and use of high precision interferometers for the measurement of thermal expansion.
- NPL: Discussion and knowledge transfer about electromechanical resonance measurements.

The REG ULE also provided an introduction to Piezoelectrics training for the project partners and gave a detailed lab tour to them during a project visit.

Two different types of samples were needed for the Electrocaloric part of the project, namely bulk and thin-film.

The bulk samples came from stakeholders, Syfer, University of Leeds and Nanoforce and came in a range of different ceramic compositions.

The thin-film samples were made by the University of Cranfield REG partner and were made in two different ceramic compositions. The devices were thin-films where the substrate they were grown on had been etched away leaving a free-standing film around 300 µm across to minimise the effect of thermal conduction in to the substrate. Two different designs of sample were produced, one with a thin-film metal resistive thermometer on top of the sample and one with no thermometer on top that was designed for measurement under the thermal camera.

4 Actual and potential impact

Dissemination activities:

The project created a Stakeholder community of more than 60 with members from across Europe and the US, with representatives from both academia, major ceramics manufacturers and industrial end users. This enabled the project to access the industrial and academic knowledge to ensure that the project delivered the most useful results.

The project held a workshop early in the project to engage the end-users to ask the stakeholders which piezoelectric measurement parameters were the ones that were most used in their sector, so that the project could focus on them. It also asked the Stakeholders for their input and comment about the initially proposed options for the sample compositions that the REG would then work to develop for the project to work on.

A project webpage (http://www.metco.npl.co.uk/) was set-up and kept regularly updated, with project news and newsletters. The initial plan was to host a Blog, but this was decided to be changed to include webinars as previous attempts at using blogs did not result in the anticipated engagement.

Three editions of a project newsletter was produced, with contributions from the project partners and stakeholders, to keep people updated on the project progress, these were emailed to stakeholders and made available via the project webpage.

Stakeholder Workshops / Webinars

To disseminate the project knowledge and engage with stakeholders in an ongoing basis a series of eleven webinars was delivered by the project partners, the topics included “High Temperature Piezoelectrics: Materials, Applications and Metrology Challenges”, “Measurement of Piezoelectric Properties at High Temperature by the Resonance Method” and “Full-field precision interferometry for measuring temperature dependence of length, strain and thermal-expansion in piezoelectric materials”, these were recorded and are available from the NPL Events YouTube page.

Technical Dissemination

The technical dissemination of the project took place through 11 posters and 13 presentations at a number of major conferences including, Piezo 2013, FRINGE, PiezoMEMS 2014 and NEWRAD 2014. The presentation at the IEEE International Symposium on Applications of Ferroelectrics by M Rokosz won the poster prize.

The industrial partner AixACCT systems also covered their project work at stands at 4 other major Piezoelectric conferences and trade fairs.

A total of 5 peer-reviewed publications were published during the project, covering all the parts of the project and demonstrating the success and outputs that had been achieved. These papers have been cited 18 times in the time since they were published, demonstrating their relevance and use to the research community.

We also produced 6 less technical articles that were aimed at a more general readership and published in well-read trade press, so that a wider audience could be reached.

Workshops and Training Courses

The University of Leeds REG undertook training at the MIKES, PTB and NPL helping him broaden his understanding on the measurements. Both REG and aixACCT provided the other project partners training on the production and existing measurement techniques for piezoelectric materials.

A one day workshop on defining a Figure of Merit for Electrocalorics was held in 2015 and attended by delegates from a number of leading academic researchers as well as the UK Knowledge Transfer Network and project partners. Agreement on future work, best practice needs and ways to quantify the uncertainties present was achieved.

Towards the end of the project a “High Temperature Piezoelectric Metrology Workshop” was held at the Piezo2015 Conference in January 2015 in Slovenia. This is one of the main biannual conferences for advances in electroactive, particularly piezoceramic, materials and devices. The training workshop provided in-depth coverage of high temperature piezoelectric measurements including resonance and interferometry, comparison of measurement methods, uncertainties and best practice. It also covered developments in high temperature piezoelectric materials from research and industry perspectives. The workshop was attended by 46 people and the presentations have been made available on YouTube for future availability.

At the end of the project we hosted a final Stakeholder meeting, presenting the results and lessons learned in the project, this was attended by 22 stakeholders and time was provided for an open discussion on the future trends and needs in the field.

The high temperature electromechanical resonance measurements extend the current scope of the EN 50324-2:2002 “Piezoelectric properties of ceramic materials and components —Part 2: Methods of measurement —Low power” Standard. A discussion was held with VAMAS (Versailles Agreement on

Materials and Standards) about adding this work into their Technical Work Item 24 as at elevated temperatures the losses in materials increases and so new guidance is needed in order to obtain accurate and repeatable measurements.

Intermediate impact

Measurement Capability

The project developed a number of new and enhanced Metrological Capabilities at both NMI and REG partners, these are now available for both further collaborative research or for commercial use by end-users. These enable the measurement of samples to be undertaken with the application of electrical excitation, where previously capability did not allow for this:

- NPL unique thermographic test facility for measuring the direct electrocaloric effect in thin film and bulk samples
- A high temperature vacuum furnace with precision Jamin interferometer, this enables the expansion of samples to be measured at temperatures up to 1000 °C. The system can also be configured to measure the self-heating of samples during testing, which is important to avoid device damage in use.
- The PTB interferometer upgrade enables full-field sample expansion to be traceably measured up to 200 °C, this is possible for both piezoelectric and more conventional samples. This facility can provide full-field sample displacement, which is able to map the actuation and distortion of samples, providing useful information to understand the performance of samples (as was demonstrated in the project).
- The LNE Thermophysical property measurement systems for measuring emissivity, enthalpy, thermal diffusivity and thermal conductivity at high temperatures. These parameters are important to understand the material performance and are needed when multi-physics modelling for device design and optimisation is needed for industrial applications.
- The work at MIKES developed a facility for measuring the high temperature emissivity of electrically excited Piezoceramics that can help with understanding their thermal performance.
- NPL and REG Leeds collaborated on the development of the high-temperature resonance measurement facility, which is now being used by Leeds for their ongoing materials research. This work and the project publications will help stimulate further development of the existing Piezoceramic testing standard that is only applicable at room temperature, where robust measurement data is needed.

Consultancy

Materials measurements have been provided to Queen Mary University of London, helping them with their research into other classes of high temperature Piezoceramics that they are actively researching for industrial application.

Industrial Uptake

The extensive materials research and development work that was undertaken by the Leeds REG will be commercialised by the University of Leeds spin-out company Ionix Advanced Technologies who have taken the REG on as a member of staff and are further expanding. Ionix are further developing the material and marketing it for industrial end use for sensing and actuation in harsh environments such as power generation and industrial processing, this will provide industry with the solutions providing a direct route to deliver the intended impacts of this project.

Ionix now manufactures a range of proprietary high performance piezoelectric materials (HPZ) for applications in high temperature, high shock and high pressure environments, and for use in sensors, actuators and transducers in aerospace, automotive and energy sectors. These materials are tested against the measurement procedures developed in METCO and indeed with the equipment developed by METCO partner aixACCT gmbh. They have also developed and launched a new high temperature ultrasonic platform, HotSense, which is used across the UK, Europe and North America for continuous ultrasonic thickness measurements at temperatures up to 400 C in oil & gas, nuclear and chemical sectors. They have also successfully completed a grant project with Rolls Royce to deliver a fuel actuator range finding system based on this system and the HPZ piezoelectric materials

The modelling, measurement and figure of merit work on Electrocalorics have provided the academic and nascent industrial users of these materials with a more robust and traceable set of measurements. This will make comparisons of materials suitability for use as solid-state cooling systems simpler and more robust.

Work has carried on with a student Maciej Rokosz working jointly with NPL and Imperial College London to undertake more work on the characterisation of potential electrocaloric materials using the thermal camera facility developed at NPL.

aixACCT systems have developed new sample mounting hardware for their two main commercial (single and double beam) piezoelectric measurement systems for bulk and thin-film sample characterisation. This will enable their customers (in academia and industry) to be able to better characterise their materials across a much wider temperature range than previously available with the confidence to know that the measurements have been compared to traceable systems at the NMI partners.

5 Website address and contact details

http://projects.npl.co.uk/METCO/

metco@npl.co.uk

6 List of publications

Publication	Partners	WP
Experimentally validated finite element model of electrocaloric multilayer ceramic structures, Smith, N.; Rokosz, M. & Correia, T. J. Apply. Phys, V116, 044511 (2014)	NPL	5
Surface mapping of field induced piezoelectric strain at elevated temperature employing full-field interferometry, T. Stevenson, T. Quast, G. Bartl, T. Schmitz-Kempen and P. M. Weaver, IEEE TUFFC Special Transactions, V62, p88-96, 2015	NPL, PTB, aixACCT	3
Piezoelectric materials for high temperature transducers and actuators, Stevenson, T. Martin, D. Cowin, P. Blumfield, A. Bell, A. Comyn, T. & Weaver, P., J. Mat. Sci. Materials in Electronics, 10.1007/s10854-015-3629-4 (2015)	NPL, REG(ULE)	6
High temperature measurement and characterisation of piezoelectric properties, P.M. Weaver, T. Stevenson, T. Quast, G. Bartl, T. Schmitz-Kempen, P. Woolliams1 A. Blumfield, M. Stewart, M.G. Cain, J Mat. Sci. Materials in Electronics, 10.1007/s10854-015-3285-8, 2015	NPL, PTB, REG(ULE), aixACCT	1
Validation of a Blackbody Comparator Based System for Thermocouple Calibration, M. Ojanen, O. Hahtela, M.Heinonen, Int. J. Thermophys, 35, p526-34 10.1007/s10765-014-1565-9 (2014)	MIKES	4