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Dielectric measurements on a novel $Ba_{1-x}Ca_xTiO_3$ (BCT) bulk ceramic combinatorial library

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Abstract High-throughput combinatorial methods have the potential to discover new materials. They can investigate the effects of a wide range of dopants on the dielectric properties to optimize existing systems, encouraging the short innovation cycles that industry requires. We are currently part of a consortium of London Universities exploring methods of producing and measuring combinatorial libraries of microwave dielectric ceramics. The London University Search Instrument (LUSI) is a fully automated, high-throughput combinatorial robot that has the potential capability to produce combinatorial libraries consisting of large numbers of sintered bulk ceramic samples with varying composition, on alumna substrates. We have reported the manufacture and characterisation of $Ba_xSr_{1-x}TiO_3$ libraries (x in steps of 0.1) as a proof of concept to demonstrate that the robot works and to confirm a compositional and functional change throughout the libraries, as well as proving that reliable measurements can be made on such small samples. Libraries of $Ba_{1-x}Ca_xTiO_3$ samples were made with varying compositions of x=0–1 in steps of 0.1, and fired to 1400 °C for 1 h, by LUSI. X-ray diffraction (XRD) data agreed with the few previous reports on this little-studied system, namely that after initially forming a solid solution with Ca addition, above $x=0.2$ a two phase system forms with values of $0.2<x<0.9$, after which a single phase system again appears with values of $x=0.9$ and higher. Dielectric measurements (100 Hz–1 MHz) showed a previously reported unusual initial increase in the Curie point with substitution up to $x=0.2$, followed by a rapid decrease to below 125 K when $x>0.4$. This initial increase has been attributed to the Ca substituting in both the Ba^{2+} A sites and the Ti^{4+} B sites of the perovskite up to $x=0.2$, after which T_c decreases greatly as the two phase system forms. Scanning probe microscopy and piezo response force microscopy (PFM) experiments also showed evidence of an increase in piezoelectricity with small amounts of x (0.1–0.2), followed by a decrease with increasing x.

Keywords Combinatorial · High-throughput · Dielectric · Ferroelectric

1 Introduction

Combinatorial materials science is the rapid synthesis and analysis of large numbers of compositions in parallel, created through many combinations of a relatively small number of starting materials. It is therefore essential that for a truly combinatorial approach that both synthesis and

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measurement must be high-throughput, to handle the large number of samples required. Combinatorial searching was initiated in the 1960s for the solid-phase synthesis of peptides by Merrifield [1], but it took until the 1990s for industry to adopt this technique, which is now deemed essential in the pharmaceutical industry, where both sample preparation and analysis are carried out by robots.

In 1970, Hanak [2] proposed his ‘multiple sample concept’ in the *Journal of Materials Science* as a way around the traditional, slow, manual, laboratory preparation procedures used to make samples for testing. Among the earliest robotic methods for ceramics was the General Electric Company Hirst Laboratories (Wembley UK) quest for cuprate superconductors [3, 4]. A series of combinatorial searches in Materials Science were carried out in 1995 by Xiang et al. [5], and after only 10 years, industry is already heavily involved in the development of this technique and the development and automation of measurements suitable for combinatorial searches.

However, to date, most high-throughput Combinatorial Materials Science uses thin films [6]. Combinatorial methods applied to bulk ceramics use either high-throughput synthesis of powders/tapes or printing methods [7], or high-throughput analysis [8], but not an integrated system including synthesis, sintering and measurement. The work reported in this paper represents initial development of a high-throughput combinatorial technique for the manufacture and measurement of sintered bulk ceramic samples. The *Functional Oxides Discovery* (FOXD) *using Combinatorial Methods* project (http://www.foxd.org, July 2007) uses high-throughput combinatorial thick-film production and screening techniques, to make bulk ceramic combinatorial libraries. The samples are made by the London University Search Instrument (LUSI; http://www.materials.qmul.ac.uk/research/facilities/lusi/, July 2007), a robot that prints samples from oxide suspensions using ink-jet printers, and also sinters the samples in a multi zone furnace at up to 1600 °C [9]. LUSI has the potential capability to produce large numbers of different sintered samples. The aim is to discover new ceramics with ferroelectric, dielectric, electronic and ionic properties advantageous to industrial users. As LUSI is unique in producing polycrystalline sintered bulk samples, it allows the examination of bulk properties, sintering, dopants, grain effects, diffusion coefficients, etc. The robot has been demonstrated to work with the successful manufacture and physical and dielectric characterisation of barium strontium titanate (BST) libraries, showing clear evidence of compositional reliability and the expected functional changes throughout the libraries, as well as demonstrating that such small samples can be measured [10, 11].

Pure $BaTiO_3$ (BT) is a well known ferroelectric and piezoelectric material, with a room temperature relative permittivity (ε_r) of several thousand. It has three phase transitions, and changes from paraelectric to ferroelectric as it undergoes the cubic ➔ tetragonal phase transition around 125 °C:

$$\textbf{Rhombohedral} \xrightarrow{\textbf{183 K}} \textbf{Orthorhombic} \xrightarrow{\textbf{273 K}} \textbf{Tetragonal} \xrightarrow{\textbf{398 K}} \textbf{Cubic}$$

Pure $CaTiO_3$ (CT) is an incipient ferroelectric, with ε_r of around 160–170, and it is orthorhombic at room temperature. Ca can be substituted for Ba throughout the whole series $Ba_{1-x}Ca_xTiO_3$ (BCT), but it does not form a simple solid solution in the way that barium strontium titanate does [12, 13]. Despite being of interest as a potential materials candidate for applications in modulators and memories [14], there has no been no systematic and comprehensive study of the dielectric properties of barium calcium titanate—the handful of papers that have characterised the bulk ceramic material have only looked at a few compositions [15] or single crystals [16]. This makes the material ideal for investigation as a combinatorial library using LUSI. Therefore, a combinatorial BCT library was manufactured by the LUSI robot, with the composition $Ba_{1-x}Ca_xTiO_3$ in steps of $x=0.1$, by automatic printing and sintering at 1400 °C by LUSI. The crystalline phases of the library were characterised by X-ray diffraction (XRD), and the dielectric properties measured over a temperature range to study the effects on Curie point, T_c. It must be stressed that the principle of combinatorial searching is to identify novel compounds which can then be optimised and characterised with more precision, and as such it is a tool to discover trends, rather than a technique intended for precise characterisation.

2 Experimental

2.1 Manufacture and electroding of samples

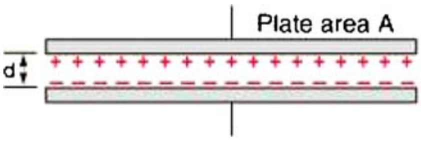
The BCT libraries were printed from aqueous ink mixtures made from $BaCO_3$, $CaCO_3$ and TiO_2 inks. The manufacture of the samples by LUSI is detailed by Pullar et al. [10]. The LUSI robot mixes materials in all possible combinations, produces samples of various configurations by ink-jet printing, and processes the samples by heat treatment, all automatically on one instrument. LUSI holds 100 alumina substrates at one time, each of which can hold 30–40 different samples as an array of small printed dots—up to 4,000 samples. A four-zone furnace is used to sinter the samples, with a maximum temperature of 1600 °C and up to 100 °C difference possible between neighbouring zones, so libraries can be simultaneously sintered at four different temperatures. A robot grabber arm transfers samples to and from the furnace, and the entire process is fully automated [17, 18]. The BCT library was sintered at 1400 °C/1 h in air.

For dielectric measurements by a contact method, both the substrate and the samples were coated with a conducting layer to form the top and bottom electrodes. Samples were first printed on silicone release paper (Grade SPT50/11, Cotek Papers Ltd., Gloucestershire, UK) to which they were non-adherent, sintered on coarse zirconia powder and then remounted onto alumina slides using silver electroding paste (M4516, Johnson Matthey, Royston, Hertfordshire, UK) and refired at 780 °C for 10 min. This provides a ground electrode. The samples were transferred between substrates using a vacuum technique that has been automated and incorporated into the LUSI robot, but it does add an extra step into the process. Therefore, we are currently developing non-contact measurement techniques, using an evanescent microwave probe to measure the dielectric properties, so the need for a ground electrode can be avoided.

After manufacture, sintering and application of the bottom electrode, the samples were polished as a complete library, and a metal contact layer was applied to the upper surface of the samples to form the top electrode using a thin layer of silver conductive paste. At this stage of development the paste was applied manually to the tops of the samples.

2.2 Characterisation methods

The morphology of the samples was observed, and silver contact areas were measured, by optical microscopy. XRD patterns of the samples were recorded in the region of 2θ= 20–75° on a PANalytical X'Pert Materials Research Diffractometer using CuK$_\alpha$ radiation, with a PANalytical X'celerator detector and a 0.5 mm footprint monocapillary in point beam mode. The X'celerator detector allows the rapid accumulation of data necessary for high-throughput analysis, achieving in <10 min a measurement that would normally take many hours. Permittivity was calculated using the parallel plate capacitor technique neglecting fringe effects, and the following equation:



$$C = \frac{k\varepsilon_0 A}{d}$$

where C = capacitance in farad, d = sample thickness in meter, k = relative permittivity (ε_r) of the sample, A = area of the upper conducting plate in square meter, and ε_0 = permittivity of free space (8.865×10^{-12} Fm^{-1}). The errors of this technique have been shown to be very low at low frequencies (<1 MHz) [19]. Accurate measurements were made of the sample height with a point gauge (±5 μm) and of the contact area under a microscope. The Curie point of the samples was measured between 135 and 500 K and at 100 Hz–1 MHz using a Precision LCR meter (HP 4284A) and an Impedance/Gain-Phase Analyzer (Solartron 1260), heating and cooling with a rate of 0.5 K min^{-1} using an environment chamber (Delta Design 9023). In the case of the dimpled samples, measurement where taken on the flat polished sections of the rim, and not in the central hollow.

A commercial scanning probe microscope (SPM; Digital Instrument, Nanoscope IIIA) was used for the piezoelectric measurements. The microscope was equipped with a lock-in amplifier and a function generator that were used to apply the alternating current and direct current (dc) voltages for both imaging and local hysteresis loop measurements. The details of the measurement set-up have been reported previously [20].

3 Results and discussion

The library consists of a series of dots around 1.5–2 mm in diameter, which have been polished for measurement, and

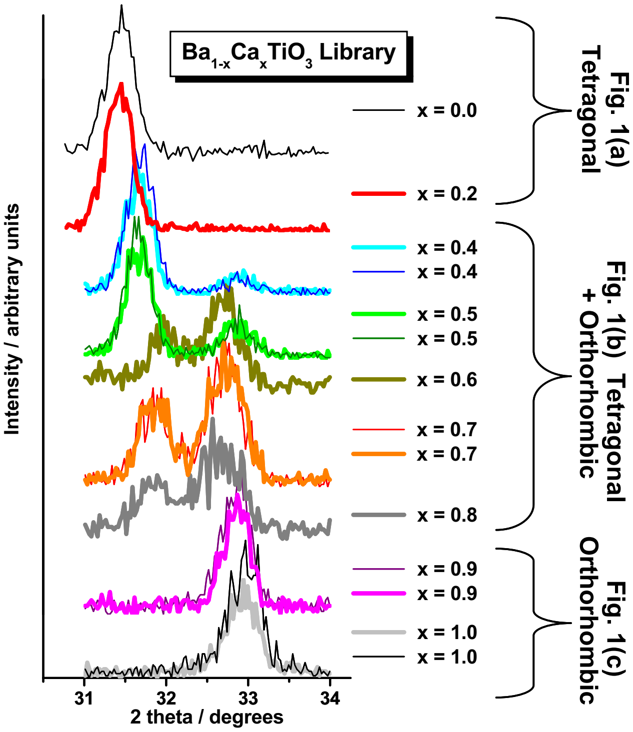


Fig. 1 XRD peaks between 2θ=31 and 34° for Ba$_{1-x}$Ca$_x$TiO$_3$ library sintered at 1400 °C. *a*, x=0.0–0.2, tetragonal phase only; *b*, x=0.4–0.8 tetragonal and orthorhombic dual phase; *c*, x=0.9–1.0 orthorhombic phase only. Two sets of data when two dots were measured

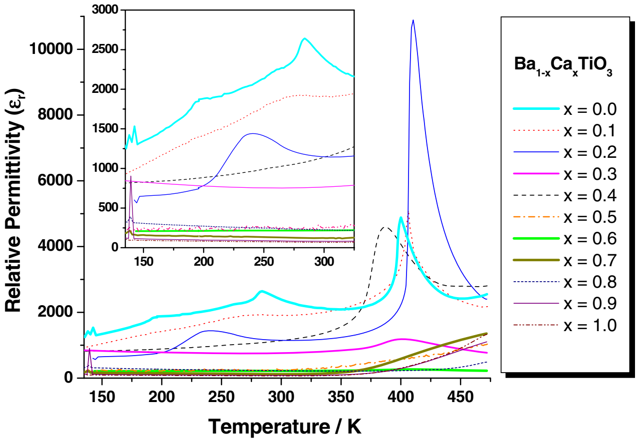


Fig. 2 Measured values of permittivity against temperature for the BCT library, measured at 100 Hz. The insert shows the data from 135 to 325 K only, for easier comparison. (The room temperature permittivity values decrease with increasing x with the exception of sample x=0.3 which was damaged during measurement; the permittivity values at the T_c peak serve only to define T_c)

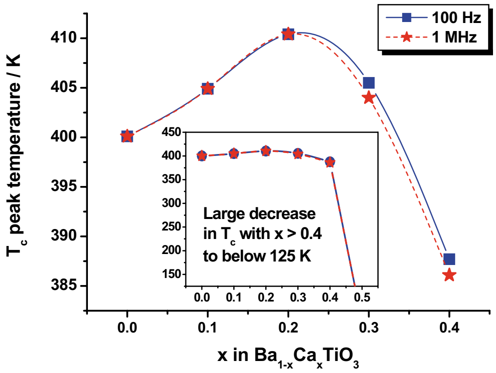


Fig. 4 Variation in Curie point, T_c, with x. *Insert* shows the large drop to below 125 K (limit of measurement) seen with x>0.4

are between 0.3 and 0.6 mm in height. Combinatorial samples can be prepared from carbonate precursors without a calcining step, as in this work. However, full density is rarely achieved on subsequent sintering because of the volumetric inefficiency associated with conversion to oxide. Although the porosity of the individual members of the library cannot be measured, they appear to be well sintered when examined by scanning micron microscopy, with only small numbers of pores apparent. The dielectric constants given in Fig. 2 are therefore affected by porosity and need adjustment, but the values of T_c, which do not depend on porosity can be accepted. The samples with high Ba content formed a "doughnut" shape, with a slight dip in the centre. This is a feature of the drying process for these particular inks, and can be avoided by optimisation of the ink composition [21]. As the Ca content increased the size of the recess in the centre decreased, and with x=0.7 and greater the dots were flat polished conical sections.

XRD measurements showed no other phases other than the expected perovskite BCT phases. The changes in the 100% intensity peaks are shown in Fig. 1. Pure BT is tetragonal, and the 100% intensity (110) peak is expected at 31.45°, whereas CT is orthorhombic and has a 100% intensity (121) peak at 33.04°. Wang et al. [13] reports that in Ba$_{1-x}$Ca$_x$TiO$_3$ a single phase tetragonal peak is seen up to the solubility limit of Ca in the tetragonal structure at x= 0.23. This is also noted in Fig. 1, a, where a single peak is observed for x=0.0–0.2, shifting to a slightly higher angle as the smaller Ca^{2+} cation is accepted into the tetragonal structure. Wang reports that tetragonal and orthorhombic phases co-exist between x=0.23–0.93. Again, this is seen in Fig. 1, b, and as the Ca content increases the proportion of the tetragonal peak decreases and the orthorhombic peak increases between x=0.3 and 0.8. Interestingly, while Wang reported that these dual phases exhibited no shift in peak position and coincided almost precisely with the peak positions for tetragonal Ba$_{0.8}$Ca$_{0.2}$TiO$_3$ and orthorhombic Ba$_{0.07}$Ca$_{0.93}$TiO$_3$ (x=0.2 and 0.93 respectively), it can be seen in Fig. 1 that there is a steady increase in 2θ for both

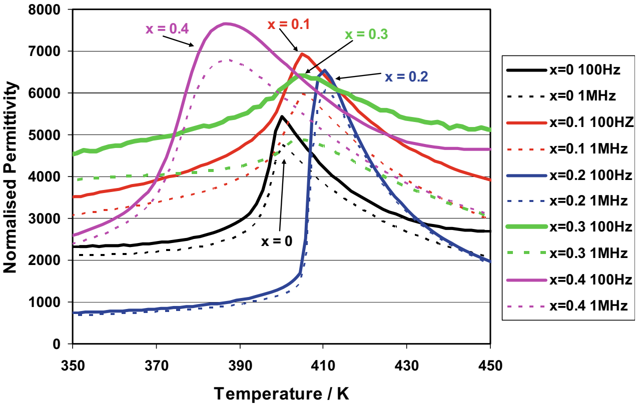


Fig. 3 Normalised permittivity values against temperature for x=0–0.4, measured between 350 and 450 K and at 100 Hz and 1 MHz

Table 1 Comparison of T_c (K) as a function of composition for LUSI results and results for BCT in previously published work (Ba$_{1-x}$Ca$_x$TiO$_3$).

X	LUSI, 100 Hz	LUSI, 1 MHz	Oxalate route [15]	Gel route [15]	Single crystal [16]
0	400.1	400.1	403	403	400
0.1	404.9	404.9	411	413	415[a]
0.2	410.4	410.4	n/a	n/a	428
0.3	405.5	404.0	408	405	n/a
0.4	387.7	386.1	403	n/a	n/a
0.5	No peak	No peak	401	395	n/a
0.6	No peak	No peak	No peak	No peak	n/a

[a] x=0.12

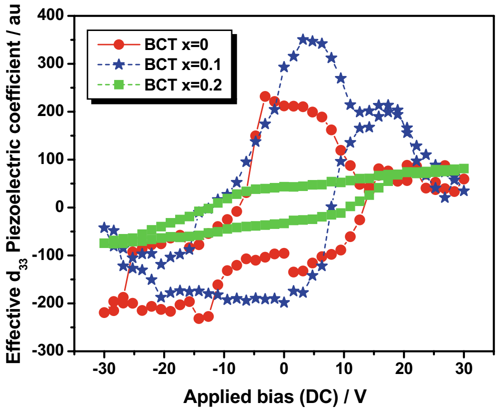


Fig. 5 Local piezo response hysteresis loops of effective d_{33} coefficient of $Ba_{1-x}Ca_xTiO_3$ combinatorial library, fired at 1400 °C

peaks as Ca content increases in our samples. This shift suggests that there may indeed be some solubility of Ca in compositions between $x=0.23$ and 0.93, although clearly a two phase system exists. Wang states that above $x=0.93$, a pure single orthorhombic phase exists, and that can be seen in Fig. 1, c, again with a slight increase in 2θ as the Ca content increases from $x=0.9$ to 1.0. The observed peak positions of the two end members of the BCT library are 31.45° for $x=0$ and 32.95° for $x=1.0$, matching almost exactly their expected values. Two BCT libraries were examined, so there are two sets of data for some values of x, where both could be measured.

Continuous measurements of permittivity vs. temperature within 135–490 K were carried out in the Delta Chamber over a range of frequencies between 100 Hz and 1 MHz. The Delta Chamber measures the capacitance using an LCR meter over a range of frequencies, while heating or cooling and accommodates eight samples at a time. Permittivity was calculated from the sample thickness and area of the upper electrode and compared with expected values. This allowed the measurement of the Curie point, T_c, of the samples, which coincides with a peak in permittivity at the paraelectric ➔ ferroelectric phase transition. Although the Delta Chamber can measure down to 125 K, below 150 K the signals become noisy and unreliable due to condensation on electrical connections. The measured values of permittivity against temperature for the BCT library are shown in Fig. 2, measured at 100 Hz. Clear T_c peaks are seen above 375 K for $x=0$, 0.1, 0.2 and 0.4, and a smaller peak for $x=0.3$. This sample was found to have cracked after measurement, which may have reduced its permittivity values. No peaks were seen for samples with $x>0.4$, and these samples also all had similarly low ε_r values. The room temperature permittivities can be seen more clearly in the inserted graph in Fig. 2, where the room temperature ε_r values for samples with $x>0.4$ are all between 100 and 250, increasing to 300 for $x=0.3$, ~1,150 for $x=0.4$ and 0.2, 1,900 for $x=0.1$ and 2,400 for $x=0$, typical of expected values for pure BT [11]. Thus pure BT has the greatest room temperature ε_r and the general trend shows a decrease with increasing calcium content.

To be able to examine and compare the T_c peaks of the samples with $x=0$–0.4 all on one curve, the permittivity values were normalised and plotted against temperature in Fig. 3 between 350 and 450 K. Although the absolute permittivities cannot be compared to each other in this figure, the peak temperatures are unaffected by this normalisation and can be compared accurately. With values of $x>0.4$, the peak was below 125 K, and could not be measured. Plots are shown for measurements at both 100 Hz and 1 MHz, to illustrate that the trends are true over a wide range of frequencies. It can be seen that the trend in T_c is unusual in this system, as found by others. The pure BT ($x=0$) has a T_c value of around 400 K as expected, but T_c then increases slightly to 405–410 K with $x=0.1$–0.2, then decreases slightly to 405 K at $x=0.3$,

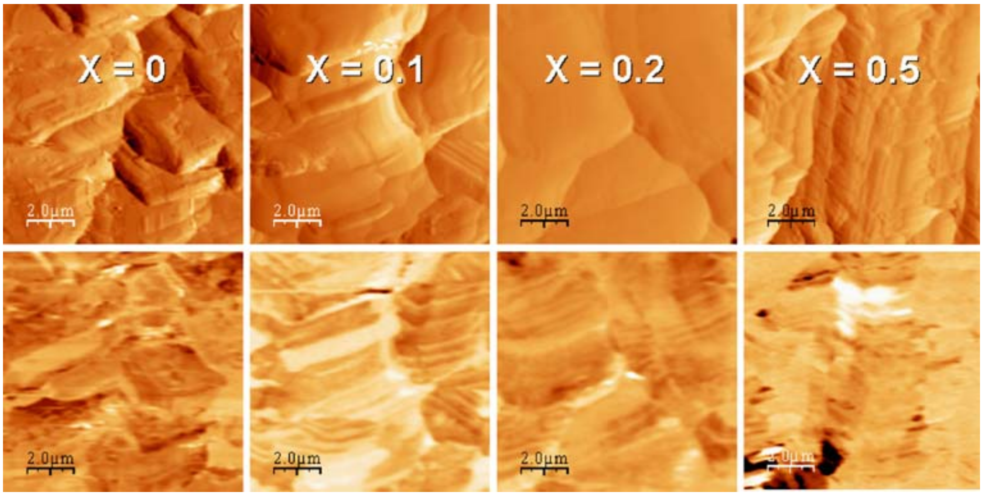


Fig. 6 SPM images of topology (*top row*) and piezo response (piezoelectric domains, *bottom row*) of $Ba_{1-x}Ca_xTiO_3$ combinatorial library, fired at 1350 °C

followed by a larger drop to 387 K at x=0.4. There is then a large decrease with values of x>0.4, and T_c cannot be measured as it is below 125 K for all such samples (Fig. 4). This non-linear behaviour of T_c has been seen before in the handful of papers reporting this material, and our data are compared to these results in Table 1. In samples made from precipitation methods ($Ba_{1-x}Ca_xTiO_3$ where x=0.05 steps up to 0.50) and sintered at 1380–1450 °C, T_c reached a maximum at ~0.1, and then decreased again [15], to just below the T_c of pure BT for x=0.45. With x=0.6 no peak could be found above room temperature, and maximum permittivities were from 10,000 for pure BT to 7,000 for x= 0.4. In BCT single crystals with x=0.12 T_c was 415 K, increasing to 428 K at x=0.2, with permittivities of around 5,000 [16]. This behaviour is explained by the Ca ions going into both the A sites and B sites of the perovskite at the start of Ca substitution, with the increase in T_c occurring as Ca atoms substitute for Ti in the B site, and the decrease in T_c beginning once no more Ca can go into the B site, when x=~0.2 [22]. This coincides with the formation of the dual phase material at x=0.23. Our T_c results are compared with the existing published data in Table 1. Wang et al. [13] only report a value for one composition, x=0.23, with T_c="lying around 120 °C" (~393 K).

Two different kinds of local measurements with SPM were performed at room temperature. First, the topography and the effective piezoelectric signal, d_{33}, were simultaneously imaged over an area of a few square micrometers. Second, piezoelectric hysteresis loops (d_{33} after the application of consecutive dc voltage pulses) were measured. No local piezo response hysteresis loops could be measured for x>0.3, suggesting this material loses its piezoelectricity as the dual phase material forms and the Ca-rich compound dominates (Fig. 5). This is contrary to the results reported by Wang et al. [13], who found that d_{33} peaked at x=0.23, dropping greatly at values above this, and steadily decreasing with x up to 0.5, the limit of their reported data. Differences may be due to the small size of these samples, differences in degree of sintering, or differences in measurement technique. The largest piezo response in our samples was from the x=0.1 sample, and even for x=0 the d_{33} values were higher than those we found in BST libraries made by LUSI [11]. The strange loop shape is caused by out-of-plane polarisation causing a loss of piezo response at higher voltages, and is often seen in piezo response force microscopy (PFM) of highly piezoelectric samples, such as pure BT. PFM of $Ba_{1-x}Ca_xTiO_3$ showed much clearer piezoelectric domains than those seen in the BST libraries [11]. These domains are best defined at x=0.1, which also had the highest d_{33} coefficient, and less apparent at x=0.2 (highest T_c), and have virtually disappeared by x=0.5 (Fig. 6).

4 Conclusions

Libraries of $Ba_{1-x}Ca_xTiO_3$ samples were made with varying compositions of x=0–1 in steps of 0.1, and fired to 1400 °C for 1 h, by LUSI, a fully automated high-throughput combinatorial robot that has the potential capability to produce large numbers of sintered bulk ceramic samples with varying composition. The XRD data agreed with the few previous reports on this little-studied system, namely that after initially forming a solid solution with Ca addition, above x=0.2 a solubility limit is reached and a two phase system is created between values of $0.2<x<0.9$, after which a single phase system again appears with values of x=0.9 and higher. The two phase system consists of Ba-rich and Ca-rich components, close in composition to the pure BT and CT end members (tetragonal and orthorhombic respectively), and the Ca-rich phase became the dominant majority phase with increasing Ca addition. No other crystalline phases were seen in the XRD spectra.

The Curie point showed an unusual initial increase with substitution up to x=0.2, followed by a rapid decrease to below 125 K when x>0.4. This initial increase has been attributed to the Ca substituting in both the Ba^{2+} A sites and the Ti^{4+} B sites of the perovskite up to x=0.2, after which T_c decreases greatly as the dual phase system forms. SPM and PFM measurements also showed evidence of an increase in piezoelectricity at low x (0.1–0.2), followed by a decrease with increasing x.

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