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Manufacture and measurement of combinatorial libraries of dielectric ceramics

Part II. Dielectric measurements of $Ba_{1-x}Sr_xTiO_3$ libraries

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Abstract

Applying combinatorial methods to materials science offers the opportunity to accelerate the discovery of more efficient dielectric ceramics. High-throughput methods have the potential to investigate the effects of a wide range of dopants on the dielectric properties, and to optimise existing systems, encouraging the short innovation cycles that the communications technology industry requires. The London University Search Instrument (LUSI) is a fully automated, high-throughput combinatorial robot that has the potential capability to produce large numbers of sintered bulk ceramic samples with varying composition in 1 day, as combinatorial libraries on alumina substrates. $Ba_{1-x}Sr_xTiO_3$ (BST) libraries were produced by LUSI as a proof-of-principle, with $x = 0$–1 in steps of 0.1, and fired to 1350 and 1400 °C for 1 h. Part I of this paper described the manufacture and physical characterisation of BST libraries, showing a regular change in composition with x across the libraries. In this second part, the dielectric properties of BST libraries produced by LUSI are assessed at frequencies between 100 Hz and 1 MHz, and at temperatures between 150 and 500 K. Local piezoelectric properties were also characterised by scanning probe microscope (SPM). All measurements showed evidence of a clear functional gradient varying with x across the library, with measured ε_r corresponding to expected values for BST.

Keywords: Combinatorial high-throughput; $BaTiO_3$ and titanates; Dielectric properties; Piezoelectric properties

1. Introduction

Combinatorial chemistry is the rapid synthesis and analysis of large numbers of molecules, through many combinations of a relatively small number of starting compounds. This was initiated in the 1960s for the solid-phase synthesis of peptides, by Robert Bruce Merrifield at Rockefeller University,[1] who later won the Nobel Prize in Chemistry in 1984 for this work. However, it took until the 1990s for industry to adopt this technique, and it is now essential for the pharmaceutical industry. Each year 10 000s of new molecules are discovered through automated high-throughput combinatorial searches, in which both sample preparation and analysis is carried out by robots.

In 1970, Joseph Hanak 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.[2] However, it took until 1995 for the first combinatorial searches in Materials Science to be carried out by Xiang et al.,[3] 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.

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However, to date most high-throughput Combinatorial Materials Science uses thin films.[4] The work reported in this paper represents the first attempts to develop a high-throughput combinatorial technique for the manufacture and measurement of sintered bulk ceramic samples. The *Functional Oxides Discovery using Combinatorial Methods* project (FOXD)[5] 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),[6] 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.[7] LUSI has the potential capability to produce large numbers of different sintered samples in 1 day. 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.

$Ba_{1-x}Sr_xTiO_3$ (BST) is a continuous solid solution between $BaTiO_3$ and $SrTiO_3$ over the whole composition range. The Curie temperature of the $Ba_{1-x}Sr_xTiO_3$ system decreases linearly with increasing amount of Sr in the $BaTiO_3$ lattice, and since the solid solution can be formed over the whole concentration range, electrical and optical properties of BST can also be tailored with different Ba/Sr molar ratios. It has been extensively measured and studied, and its properties are well documented for a wide range of compositions. Pure $BaTiO_3$ (BT) has three phase transitions, and changes from paraelectric to ferroelectric as it undergoes the cubic ➔ tetragonal phase transition around 125 °C:

183 K 273 K 398 K
Rhombohedral ➔ Orthorhombic ➔ Tetragonal ➔ Cubic

As strontium is substituted for barium, this paraelectric ➔ ferroelectric transition temperature (the Curie point) lowers, reaching room temperature at $x = 0.37$. BST has useful dielectric properties, and is of interest to industry for a wide range of applications from low to microwave frequencies (GHz).[8] BST has a high relative permittivity (ε_r), and both ε_r and operating frequency are also tuneable by applying an electric field, offering a unique opportunity for the development of various microwave devices, such as microstrip line phase shifters, tuneable filters and high-Q resonators. This makes the material ideal for an initial proof-of-principle investigation using LUSI. Therefore, a combinatorial BST library was manufactured by the LUSI robot.

This paper is the second part of a two-part paper submitted to the *Journal of the European Ceramic Society*, and it details the measurement of the dielectric and piezoelectric properties of the BST arrays, and the variation of those properties with composition. 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

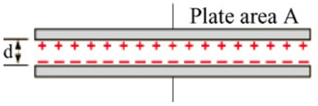
The BST arrays were printed from aqueous ink mixtures made from $BaTiO_3$ and $SrTiO_3$ inks. The manufacture of the samples by LUSI (London University Search Instrument) is detailed in part one of this paper, along with the physical characterisation of the BST libraries.[9] In short, the LUSI robot 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, each of which can hold 30–40 different samples as an array of small printed dots—up to 4000 samples, which can be printed and sintered in 24 h. 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 furnace, and the entire process is fully automated.[10,11]

For dielectric measurements by contact, both the substrate and the samples had to be coated with a conducting layer to form the top and bottom electrodes. The bottom electrode was placed on the substrate, under the samples. Initially the alumina substrates were coated with frit-free platinum paste (Ferro GmbH, product code 6402 1001, Hanau, Germany) by brushing. After air drying, the paint was fired at 1300 °C for 1 h. Three coatings were made to ensure the film was conductive throughout. However, there were problems with sample adhesion after printing, and platinum may react with materials containing bismuth or zinc, both of which feature in many promising dielectric and ferroelectric compositions. Samples were first printed on silicone release paper (Grade SPT50/11, Cotek Papers Ltd., Glos, 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, Herts, 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 flat as a complete library, and a metal contact layer was applied to the upper surface of the samples to form the top electrode by one of two methods. LUSI001 (which was fired at 1400 °C for 1 h) had a thin layer of silver conductive paste applied by hand to the tops of the samples. LUSI002 (which was fired at 1350 °C for 1 h) had a 0.5 μm layer of Ag/Ti deposited on the samples using a shadow mask on an e-beam evaporator (Kurt J. Lesker, USA). Both sets of samples were measured and compared.

2.2. Characterisation methods

The morphology of the samples was observed with a Hitachi S-4300 Scanning Electron Microscope (SEM). Dielectric measurements at 100 Hz and room temperature were carried out on a Signatone Probe Station. The capacitances of the samples were measured using a HP 4263B LCR meter at 100 Hz, and at 22 °C. Short and open circuit calibrations were carried out to ensure that the measurement errors were <1 per cent, and errors in capacitance were ±1 pF. Permittivity was calculated using the parallel plate capacitor technique, and the following equation:



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

where C = capacitance in F, d = sample thickness in m, k = relative permittivity (ε_r) of the sample, A = area of the conducting plates in m^2, and ε_0 = permittivity of free space (8.865×10^{-12} F m^{-1}). The effect of electrode fabrication is discussed in Section 3. The errors of this technique have been shown to be very low at low frequencies (<1 MHz).[12] The Curie point of the samples was measured between 150–500 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).

A commercial SPM (DI, 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 ac and dc voltages for both imaging and local hysteresis loop measurements. The details of the measurement setup have been reported previously.[13]

3. Results and discussion

The $Ba_{1-x}Sr_xTiO_3$ libraries were printed as arrays of 11 pairs of dots, 2 of each composition from x = 0–1 in 0.1 steps, on each slide. These were fired by LUSI at 1350 and 1400 °C for 1 h (Fig. 1). When sintered at 1350 °C the pure BT samples (x = 0) had large grains up to 20 μm in diameter (Fig. 2), but these grains became smaller with increasing x, and at x = 0.2 and x = 0.3 were <5 μm in diameter (Fig. 3). When fired at 1400 °C for 1 h there was no significant increase in grain size compared with the 1350 °C samples, but the x = 0 and x = 0.1 samples began to develop cracks. Confirmation of the composition of the libraries in the BST arrays was given in the first part of this article.

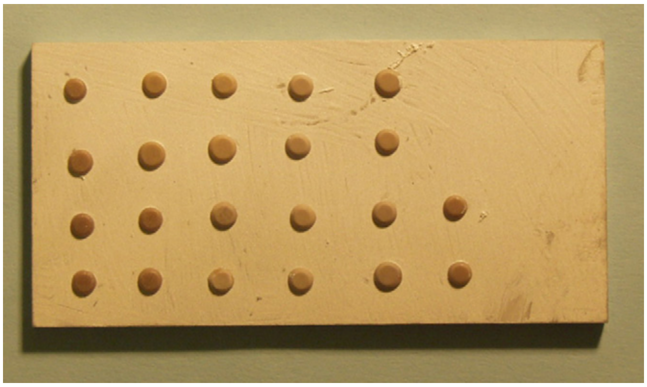


Fig. 1. Printed and sintered LUSI $Ba_{1-x}Sr_xTiO_3$ array. Eleven pairs of dots with varying composition from x = 0–1 in 0.1 steps. The dots are ∼2 mm in diameter, and these have been polished.

Capacitance measurements were made on the two BST libraries, LUSI001 and LUSI002. Each sample had two dots for each value of x in $Ba_{1-x}Sr_xTiO_3$, and the measured values are given for both sets A and B in Table 1. The absence of data indicates that a dot was missing from the library, accidentally removed during polishing. Fig. 4 shows the plots of permittivity versus composition for all samples. The results show a clear trend of decrease in permittivity with increasing x, as the composition moves from BT ($\varepsilon_r > 2000$) to ST ($\varepsilon_r \sim 300$). The capacitance method is notoriously inaccurate for very thin samples, but for these bulk samples the errors due to sample thickness should be approximately the same as for other bulk measurements. Indeed, the results agree with expected values, as shown by a selection of previously reported data for bulk BST samples produced by standard methods given in Table 2.[14–17] There is good reproducibility between the sets of dots A and B in each library, and similar trends are seen in the two separate BST libraries. The peak in ε_r seen for the x = 0.3 sample is because this is the nearest to the composition which has a room temperature Curie point (T_C = 298 K for x = 0.37, measurement room temperature was 308 K on day of measurement). As the

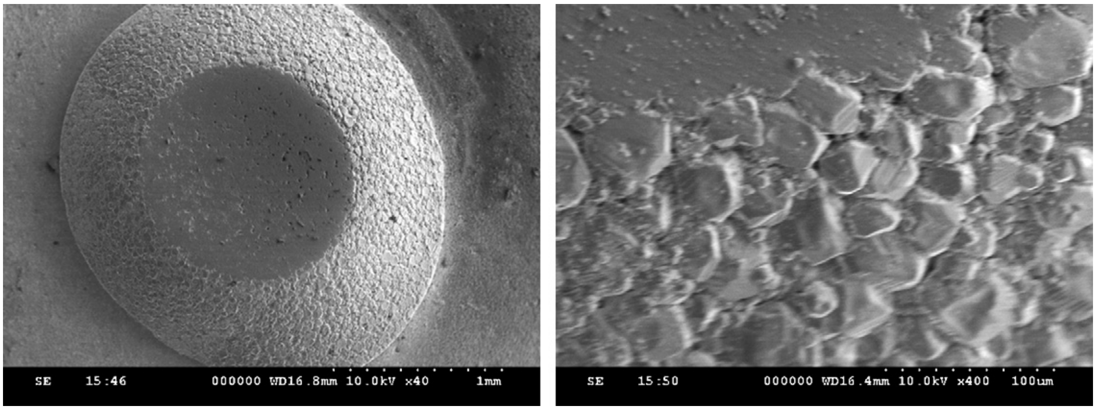


Fig. 2. SEM images of polished x = 0 (pure BT) sample sintered at 1350 °C for 1 h.

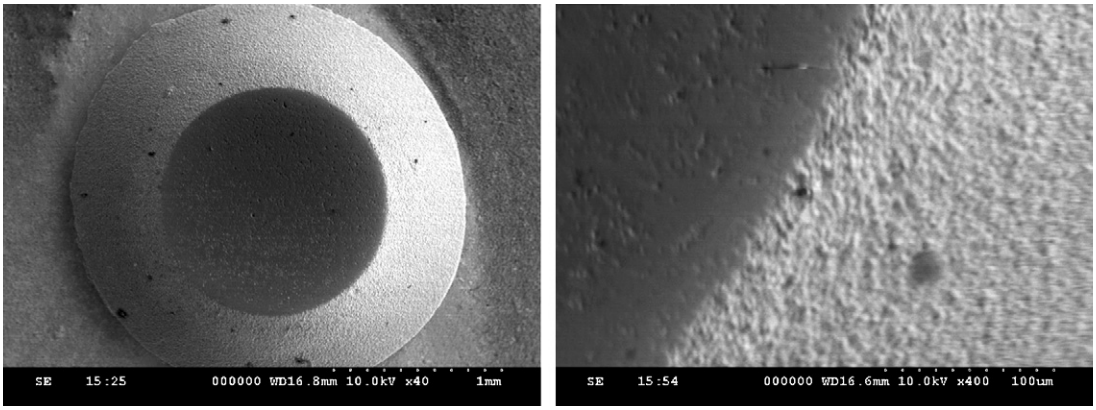


Fig. 3. SEM images of polished $x = 0.3$ ($Ba_{0.7}Sr_{0.3}TiO_3$) sample sintered at 1350 °C for 1 h.

Table 1
Area of upper electrode (A), measured capacitance (C) and calculated permittivity (ε_r) for LUSI001, fired at 1400 °C for 1 h and hand coated with silver conducting paste, and LUSI002, fired at 1350 °C for 1 h and sputter-coated with a layer of Ag/Ti 0.5 μm thick

x	LUSI001 set A			LUSI001 set B			LUSI002 set A			LUSI002 set B		
	A ($\times 10^{-7}$ m^2)	C (pF)	ε_r	A ($\times 10^{-7}$ m^2)	C (pF)	ε_r	A ($\times 10^{-7}$ m^2)	C (pF)	ε_r	A ($\times 10^{-7}$ m^2)	C (pF)	ε_r
0	2.75	72	1479	–	–	–	0.64	35	3088	0.80	40	2824
0.1	2.75	80	1643	2.03	56	1558	0.89	43	2728	0.84	39	2622
0.2	2.24	65	1639	3.14	95	1709	0.96	47	2765	1.12	50	2521
0.3	3.33	149	2527	2.93	145	2795	1.11	74	3765	1.01	68	3802
0.4	1.65	24	821	1.99	56	1589	0.62	17	1548	0.43	10	1313
0.5	–	–	–	6.15	164	1506	1.54	58	2127	0.88	34	2182
0.6	1.09	26	1347	1.54	31	1137	0.93	21	1275	0.62	17	1548
0.7	1.72	22	722	2.01	30	843	0.74	18	1374	0.90	13	816
0.8	1.41	15	601	1.61	18	631	0.68	12	997	1.01	13	727
0.9	1.70	15	498	1.74	16	519	0.92	9	552	–	–	–
1.0	1.41	9	360	1.65	11	376	1.02	8	443	0.97	8	466

Two sample dots for each composition, making two sets of results, A and B.

phase transition from paraelectric to ferroelectric occurs, a sudden peak in ε_r is observed. The samples electroded with silver paste give lower permittivity values than the sputter-coated samples. This could be due either to parasitic inductance, caused by finite current flowing from probe station tip and through the electrode, which was thicker in the Ag coated layer, or due to the higher sintering temperature of the coated array. These results prove that permittivity of the very small sample dots of the LSUI combinatorial libraries can be measured,

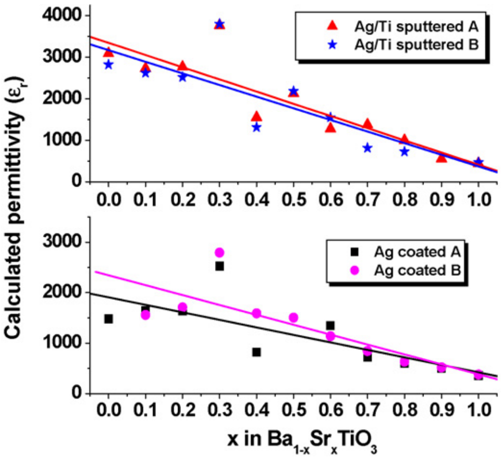


Fig. 4. Change in permittivity (measured at 308 K) with composition for Ag/Ti deposited samples fired to 1350 °C, and Ag paste coated samples fired to 1400 °C. Each library has two sets of samples, A and B. Lines represent linear fit of the data.

Table 2
A selection of previously reported room temperature ε_r values for bulk BST

x	ε_r	F (kHz)	Notes	Reference
0	9000	1	Taken at 322 K	17
0.25	2080	1	Sintered at 1230 °C	14
	2300	1	Sintered at 1230 °C	15
	1873	1	Sintered at 1260 °C	14
	1200	1	Sintered at 1260 °C	15
0.5	928	1	Sintered at 1230 °C	14
	998	1	Sintered at 1230 °C	15
	1077	1	Sintered at 1260 °C	14
	1115	1	Sintered at 1260 °C	15
	1430	100		16
0.625	685	100		16
0.75	320	1	Sintered at 1230 °C	14
	237	1	Sintered at 1230 °C	15
	314	1	Sintered at 1260 °C	14
	310	1	Sintered at 1260 °C	15
	395	100		16
0.9	249	1	Sintered at 1230 °C	15
	225	1	Sintered at 1260 °C	15
1	239	100		16

despite the dangers of fringe capacitance effects in such small samples.

Continuous measurements of permittivity versus temperature from 150 to 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 is calculated from the sample thickness and area of metal contact, and assuming that the sample is fully dense for comparison to the expected values. This allowed the measurement of the Curie point, T_C, of the samples, which coincides with a peak in permittivity at the phase transition.

As can be seen in Fig. 5, the peak temperature steadily decreases with increasing x as expected, and samples with $x = 0.8$ or greater had peaks below 150 K (pure ST has no peak, as it has no ferroelectric phase transition down to 0 K). The $x = 0.1$ trace shows a broad peak, and so is possibly not a totally pure phase. The $x = 0.4$ peak has a large shoulder that matches the $x = 0.5$ peak, suggesting that this is a mixed phase. As expected, a decrease in measured permittivity was seen at higher frequencies. Maximum reported ε_r values are around 10 000–12 000 for pure BT,[18] compared with 9500 for our sample at 100 Hz. The variation in T_C with x is shown in Fig. 6. T_C should be at room temperature (298 K) at $x = 0.37$, and the decrease should be approximately linear. As can be seen in Fig. 7, our results show good agreement with previously published T_C data for BST ceramics made by standard preparative routes.[17–19] The largest deviation from previous data was for $x = 0.1$, which was a broad, possibly mixed phase, peak, but this is still close enough to expected values for the purposes of combinatorial searches. This confirms that the trend in permittivity of the $Ba_{1-x}Sr_xTiO_3$ library is as expected, and that sample libraries can be accurately made in 10 per cent steps by the LUSI robot.

Two different kinds of local measurements with SPM were performed. First, the topography and the effective piezoelectric signal, d_{33}, were simultaneously imaged over an area of a few μm^2. Second, piezoelectric hysteresis loops (d_{33} after the application of consecutive dc voltage pulses) were measured. PFM hysteresis loops of well sintered BST (LUSI006) samples showed a steady decrease in d_{33} with increasing x in $Ba_{1-x}Sr_xTiO_3$ (Fig. 8), as expected, as pure BT is very piezoelectric and pure ST is not piezoelectric. PFM loops are often not very smooth, as the influence of surface layers and states, PFM tip materials, contamination, and orientation of domains can all affect the quality of PFM loops. Although the piezo-

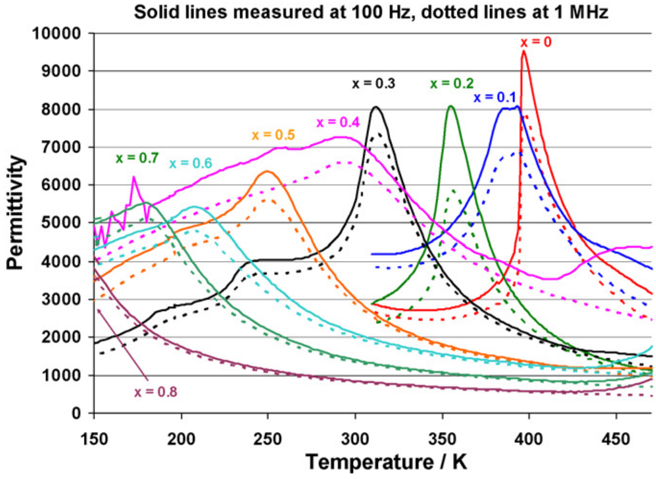


Fig. 5. The variation in permittivity with temperature for $Ba_{1-x}Sr_xTiO_3$, the peak in ε_r occurring at the Curie point (T_C). T_C should be at RT (298 K) at $x = 0.37$, and the decrease should be roughly linear.

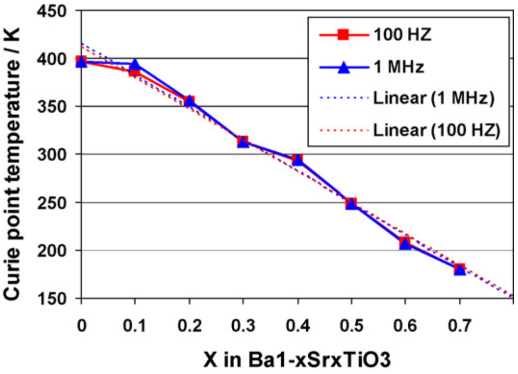


Fig. 6. Variation in Curie point temperature with x. Dotted lines represent linear fit to data.

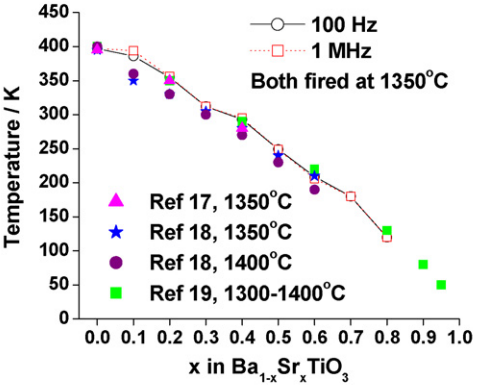


Fig. 7. Comparison of T_C results for LUSI combinatorial BST libraries (fired at 1350 °C) to previously published T_C temperature data for $Ba_{1-x}Sr_xTiO_3$.

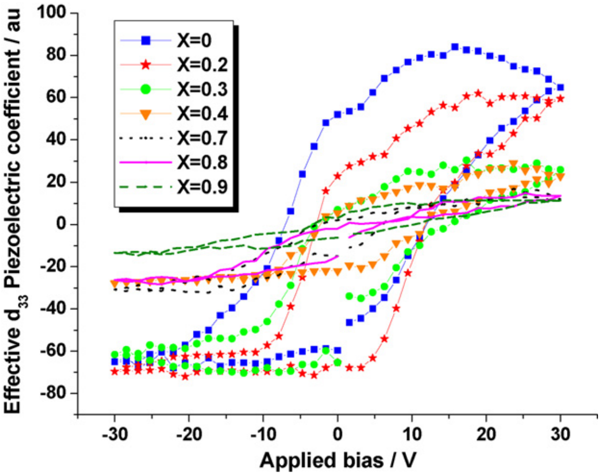


Fig. 8. PFM hysteresis loops of effective d_{33} coefficient of $Ba_{1-x}Sr_xTiO_3$ combinatorial library, fired at 1350 °C.

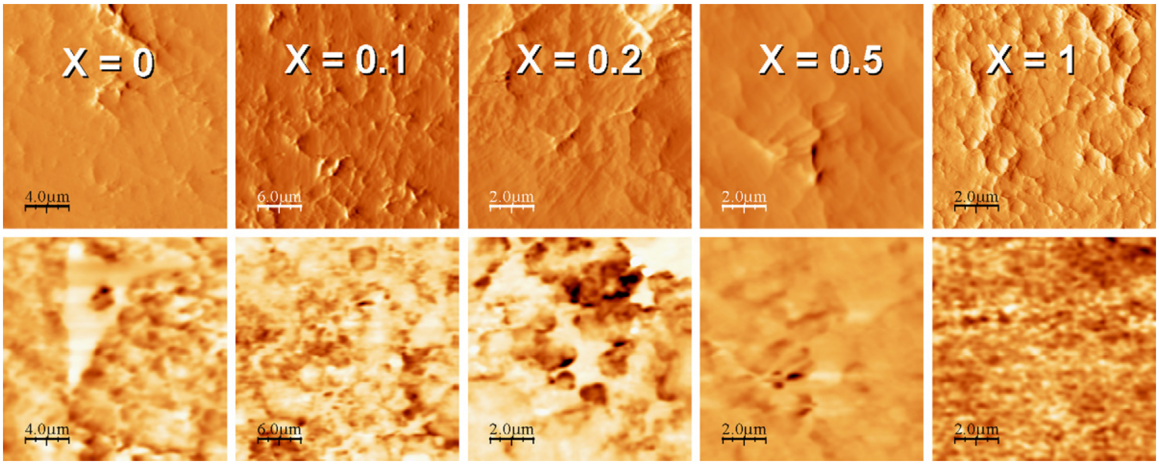


Fig. 9. SPM images of topology (top row) and piezo response (piezoelectric domains, bottom row) of $Ba_{1-x}Sr_xTiO_3$ combinatorial library, fired at 1350 °C.

electric domains are not clearly defined in the SPM images (Fig. 9), there are clear areas of contrast that are not due to morphology at $x < 0.5$, and no piezoelectric response is evident for $x > 0.4$.

4. Conclusions

LUSI is a fully automated high-throughput combinatorial robot that has the potential capability to produce large numbers of sintered bulk ceramic samples with varying composition in 1 day. As a proof of principle, libraries of $Ba_{1-x}Sr_xTiO_3$ samples were made with varying compositions of $x = 0–1$ in steps of 0.1. Fired to 1350 °C for 1 h, the samples appeared well sintered, but when fired at 1400 °C, samples with a higher Ba content showed signs of cracking, and even at 1350 °C the $x = 0$ and 0.1 samples had much larger grain sizes of up to 20 μm. Dielectric measurements (100 Hz–1 MHz) showed evidence of the compositional trends with change in composition, x, with measured ε_r corresponding to expected values. Despite the inherent errors in such measurements, these values also corresponded well to previously published bulk BST data. Samples fired to 1400 °C and coated with a thicker conductive layer exhibited a lower permittivity at all temperatures, but whether this is due to over sintering or inductive losses is uncertain. Measurements of permittivity over a temperature range of 150–500 K for libraries fired to 1350 °C exhibited a change in the Curie point that closely matched previously published data for samples made by standard ceramic routes. SPM and PFM measurements also showed clear evidence of a decrease in piezoelectricity with increasing x. These results demonstrate two important findings:

1. The BST libraries exhibit clear evidence of property variations consistent with change in composition and values close to those reported in the literature.
2. The small individual samples (1–2 mm diameter) that make up the combinatorial libraries can be measured to within a degree of accuracy acceptable for the characterisation of combinatorial searches.

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