Manufacture and measurement of combinatorial libraries of dielectric ceramics
Part I: Physical characterisation of $Ba_{1-x}Sr_xTiO_3$ libraries

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Abstract

The application of 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 1000's of sintered bulk ceramic samples with varying composition in 1 day, as combinatorial libraries on alumna substrates. The LUSI robot was demonstrated to be able to automatically print and sinter libraries of bulk ceramic $Ba_{1-x}Sr_xTiO_3$ (BST), for $x = 0$–1 in steps of 0.1. The samples were prepared from inks consisting of suspensions of $BaTiO_3$ and $SrTiO_3$ nanopowders, stabilised with 1.2 wt% dispersant. The samples were printed as arrays of 22 2 mm diameter dots, two of each composition, on alumina substrates. These were then sintered at 1350 and 1400 °C/1 h by LUSI. EDXA and XRD confirmed the compositional gradient throughout the libraries, and SEM showed the samples to be well sintered, with a large 20 μm grain size for pure $BaTiO_3$ decreasing rapidly for increasing x values.
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1. Introduction

The discovery of new dielectric materials, and the optimisation of existing ceramic systems, is limited by the time consuming process of producing and analyzing samples. This innovation cycle can be greatly accelerated by the application of high-throughput combinatorial methods. 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 1960's 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 1990's for industry to adopt this technique, although it is now essential for the pharmaceutical industry. Each year tens of

thousands of new molecules are discovered through automated high-throughput combinatorial searches, in which both sample preparation and analysis is carried out by robots.

Joseph Hanak proposed his 'multiple sample concept' in 1970, in the *Journal of Materials Science*, as a way around the traditional, slow, manual, laboratory preparation procedures,[2] but it took until 1995 for the first combinatorial searches in materials science to be carried out by Xiang et al.,[3] on luminescent materials obtained by co-deposition of elements on a silicon substrate. Since then the interest in combinatorial materials science searches has increased greatly,[4,5] to the extent that there are now conferences on this specific field,[6,7] 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.[8] The work reported in this paper represents the first attempts to develop a high-throughput

combinatorial technique for the manufacture and measurement of bulk ceramic samples. The *Functional Oxides Discovery using Combinatorial Methods* project (FOXD; http://www.foxd.org) uses high-throughput combinatorial thick-film production and screening techniques, with samples printed made using thick film technology. The project is a consortium between four London Universities; London South Bank University (LSBU), Queen Mary, University of London (QMUL), Imperial College and University College London. The samples are made by the London University Search Instrument (LUSI),[9] 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.[10] LUSI has the potential capability to produce thousands 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, this will allow us to examine 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 $Ba_{1-x}Sr_xTiO_3$ system decreases linearly with the increasing amount of Sr in the $BaTiO_3$ lattice, and has been extensively measured and studied and its physical and electrical properties well documented for a wide range of compositions. This makes the material ideal for an initial proof-of-concept investigation using LUSI. Therefore, a combinatorial BST library was manufactured by the LUSI robot. This paper details the manufacture and physical characterisation of $Ba_{1-x}Sr_xTiO_3$ BST arrays, containing a library of sintered polycrystalline bulk ceramic samples with $x = 0$–1 in steps of 0.1. A later paper will discus the dielectric properties of these materials.

2. Experimental

2.1. Manufacture of BST samples by London University Search Instrument (LUSI)

LUSI manufactures samples as compositionally and functionally gradient ceramic libraries by a method utilising thick-film ceramics technology,[10] based around an aspirating-dispensing ink-jet printer. LUSI consists of a large gantry robot with an aspirating-dispensing ink-jet printer, which can both mix compositions from a selection of inks in target well plates and print samples. As inks it can use ceramic suspensions as well as sols and solutions, and can print 10 nL drops. Thus, systems with mixtures of a large number of components can be made in the target well plates. Each dispensing cycle can aspirate up to 250 μL of ink, which is the maximum capacity of microsyringes. These are printed onto alumina substrates, which are robotically loaded into a four zone furnace capable of four concurrent heating schedules. Samples can then be loaded onto a high resolution measurement table to be addressed by contact or non-contact measurement probes, and a linked computer database holds the compositional, processing and measurement data.

LUSI will be able to do five tasks in sequence:

(1) Mix materials in all possible combinations.
(2) Produce test samples of almost any configuration by ink-jet printing.
(3) Process the samples by heat treatment.
(4) Make measurements on those samples.
(5) Store the composition, processing and measurement data in a large relational database.

Currently, only the first three tasks are carried out automatically by LUSI on dielectric ceramic samples (Fig. 1).

The printing station holds 100 25 mm × 75 mm alumina substrates, each of which can hold up to 100 different samples as an array of small printed dots, up to 10,000 samples depending on the dot size. 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. A robot grabber arm transfers samples to and from furnace, and will also move samples to the measurement table and into storage. The entire process is fully automated, and LUSI has the potential capability to make and process up to 10,000 different samples in 1 day.

When ceramic ink-jet printing is applied in combinatorial research, ink dispersion stability is more important and demanding than it is in conventional ceramic ink-jet printing where normally only one ink is used and the focus is to create complex three-dimensional objects. For combinatorial printing, preparation of well dispersed and highly stabilized ceramic inks is extremely critical, as it directly affects the composition of the mixture made. If sedimentation occurs in an un-stabilized ink, large agglomerates settle down more quickly, and accordingly the ink concentration keeps changing simultaneously, which makes it impossible to control composition precisely and obtain the right ceramic combinations. Microstirrers are brought in to avoid sedimentation and facilitate ink mixing. Mixing and printing takes several hours. Preparing a highly stable ceramic ink suitable for reliable long time-scale printing and suitable for process automation and mass production is a critical but challenging task, and at present is the rate-limiting step in the manufacture of new compositions. The BST arrays were sintered by LUSI at 1350 and 1400 °C/1 h, and the individual samples were 2 mm diameter dots that were polished to a height of 0.5 mm.

2.2. Characterisation methods

The size distributions of the ceramic powders used for making inks were measured using a Malvern Zetasizer Nano ZS (Malvern Instruments, UK). A high-energy Dyno mill (Model KDLA, Glen Creston, Ltd., Middlesex, UK) with 1 mm diameter zirconia grinding media was used to reduce particle size of the starting powders. The inks were pumped through the mill 15 times to give a total milling time of approximately 60 min. The milling temperature was less than 50 °C. A Micromeritics Gemini 2360 (Norcross, Georgia, USA) BET surface area analyser was employed to determine the surface area changes using pre and post milling powders. Samples were first degassed at 200 °C for 1 h. The dry and degassed samples were then analysed using
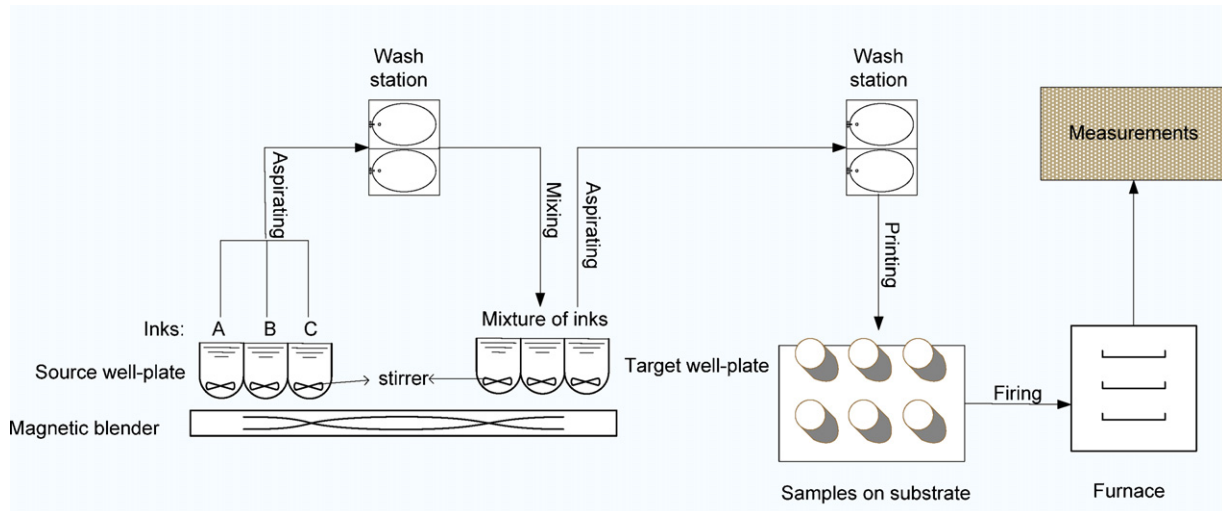
Fig. 1. Operational scheme of the combinatorial printing and firing process of the LUSI robot.

the five-point adsorption method for measuring the surface area (m^2/g). Nitrogen gas was used as the adsorbent in this technique. Particle size was estimated from surface area using the following equation:

$$d = \frac{6}{SA \times 1 \times 10^6 \times \delta}$$

where SA is the surface area in $m^2\,g^{-1}$, δ the density in $g\,cm^{-3}$ and d is the average particle diameter in m. To screen the best dispersant, sedimentation tests were evaluated on 1 vol% suspensions of oxide powders, in which different dispersants were dispersed using a 10 min treatment with an ultrasonic probe (Model U200S-Control, IKA Labortechnik Staufen, Germany). The status of each sedimentation tube was recorded for 72 h. Suspensions with least sedimentation were considered as an indication of best dispersion stability. To discover the optimum amount of the dispersant, sedimentation tests were conducted on the milled powders with a ladder of dispersant dosage levels. Suspensions with least sedimentation were again considered as an indication of best dispersion stability. The morphology of the samples was observed with a Hitachi S-4300 scanning electron microscope (SEM).

X-ray diffraction patterns of the samples were recorded in the region of $2\theta = 20$–$75°$ on a PANalytical X'Pert MRD diffractometer using Cu Kα radiation, with a PANalytical X'celerator detector and a 0.5 mm footprint monocapillary in point beam mode. The results were analysed and manipulated using PANalytical X'Pert software. 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. Scanning electron microscopy (SEM) was carried out on a Hitachi S-4300, equipped with an energy dispersive X-ray spectrometer (Oxford Instruments INCA system). Energy dispersive X-ray analysis (EDXA) was carried out with this on C coated and uncoated polished samples, calibrated with high purity copper, at an accelerating voltage of 15 keV.

3. Results and discussion

3.1. Manufacture of BST arrays on LUSI

The BST arrays were printed from aqueous ink mixtures made from $BaTiO_3$ and $SrTiO_3$ inks, the ceramic powders are both from Alfa Aesar. The BT powder was 99.7% pure with a density of $5.85\,g\,cm^{-3}$ and a measured average particle size of $1.5\,\mu m$, while the ST powder was >99% pure, with a density of $4.81\,g\,cm^{-3}$ and a measured average particle size of $1.0\,\mu m$. To reduce their particle size, the powders were milled on a high-energy Dyno mill for 1 h, after which surface areas were measured to be $20\,m^2\,g^{-1}$ for both powders. This translated as particle sizes of ST = 62 nm and BT = 51 nm after milling. The milled powders were stored in bottles on a roller table.

Seven commonly used dispersants suitable for application on oxide surfaces in aqueous media were tested as candidates. They were: Dispex A40, Darvan C, 811 and 821A, Solsperse 20K, 27K and 40K. Dispersions were made in distilled water; therefore, solubility of those dispersants in distilled water was tested at first. To find the best dispersant, sedimentation tests were evaluated on 1 vol% suspensions of BT and ST with different dispersants. Dispex A40 (density = $1300\,kg\,m^{-3}$), Darvan C (density = $1110\,kg\,m^{-3}$) and Darvan 821A (density = $1160\,kg\,m^{-3}$) were all found to be are quite effective at forming a stable and well dispersed suspension, and any one of these could be added as 4 wt% to oxides in the BT and ST ink mixtures.

The $Ba_{1-x}Sr_xTiO_3$ libraries were printed as arrays of 11 pairs of dots of ~2 mm diameter, two of each composition from $x = 0$ to 1 in 0.1 steps, on each slide (Fig. 2). When sintered at 1350 °C the pure BT samples ($x = 0$) had large grains up to 20 μm in diameter (Fig. 3), but these grains became smaller with increasing x, and at $x = 0.2$ and 0.3 had become <5 μm in diameter (Fig. 3). When fired at 1400 °C/1 h there was no obvious increase in grain size, but the $x = 0$ and 0.1 samples begun to develop cracks. In future, we shall investigate samples fired at lower temperatures. It can also been seen that the samples all appear well sintered.
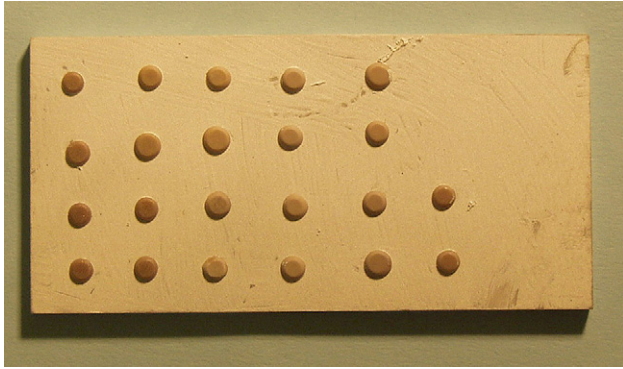
Fig. 2. Printed and sintered LUSI $Ba_{1-x}Sr_xTiO_3$ array. Eleven pairs of dots with varying composition from $x = 0$ to 1 in 0.1 steps. The dots are $\sim$2 mm in diameter, and these have been polished.
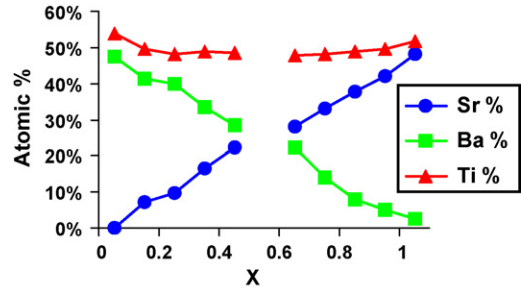

Fig. 4. Atomic% values for Ti, Ba and Sr with x from EDXA of an uncoated $Ba_{1-x}Sr_xTiO_3$ array. The $x = 0.5$ sample was missing.

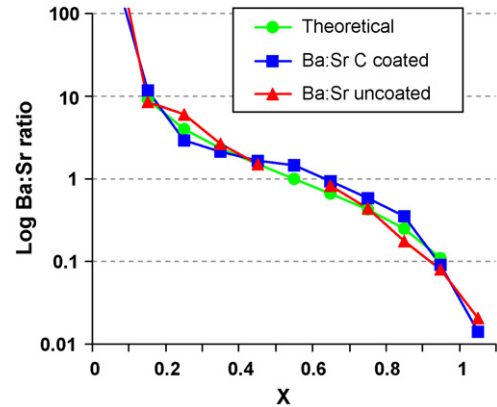Fig. 5. Log of measured and predicted Ba:Sr ratios from EDXA for $Ba_{1-x}Sr_xTiO_3$ arrays.

EDXA analysis confirmed the composition of the library for varying compositions of x to a reasonable degree (Fig. 4), in which Ti should be a constant 50 atomic% and Ba decreases as Sr content increases. Both dots for $x = 0.5$ were missing from this array, so there is a gap in data. It should be noted that the Ba Lα (4.467 keV) and Ti Kα (4.510 keV) lines have very similar energies and overlap heavily, so it is difficult to accurately measure these two atoms together by EDXA. Therefore, the ratios of Ba:Sr for a C coated and an uncoated array are shown in Fig. 5, and compared to the predicted theoretical ratio for each value of x. It can be seen that they are in very good agreement.

In Fig. 6, the 100% XRD peak for BST is shown for values of x (both $x = 0.1$ and 1 were missing from this array), on a library fired to 1350 °C. The dotted lines represent the expected values for pure BT (31.50°) and ST (32.45°). A clear shift in peak position can be seen representing the reduc-

tion in lattice parameter as Ba is replaced by Sr at increasing values of x. Fig. 7 shows a plot of variation in the centre peak position versus x, and a clear linear relationship is seen.
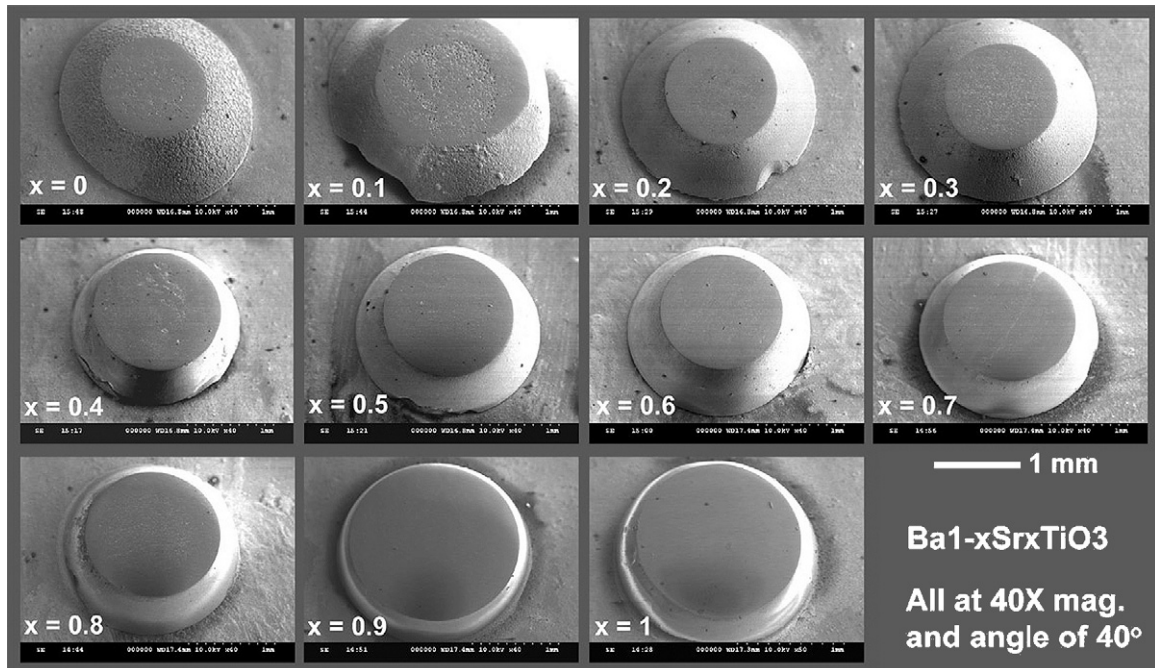

Fig. 3. SEM images of polished $Ba_{1-x}Sr_xTiO_3$ library, sintered at 1350 °C/1 h. The 1 mm scale bar shown is valid for all images, taken at the same magnification.
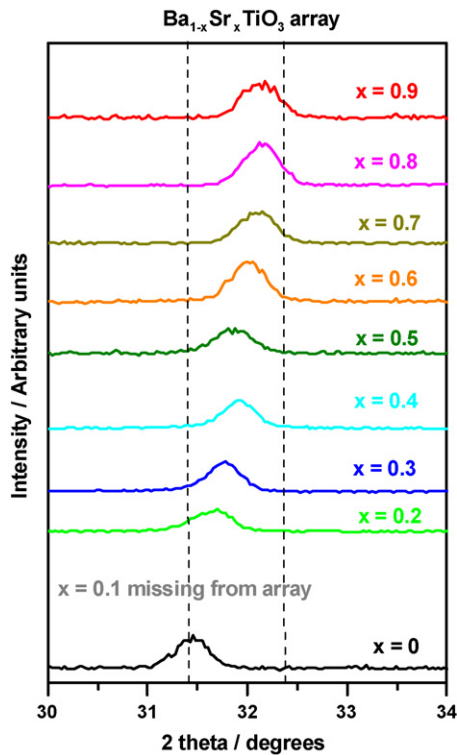
Fig. 6. XRD spectra for 100% peak of $Ba_{1-x}Sr_xTiO_3$ for values of x (both $x = 0.1$ and 1 were missing from this array), on a library fired to 1350 °C. The dotted lines represent the expected values for pure BT (31.50°) and ST (32.45°).
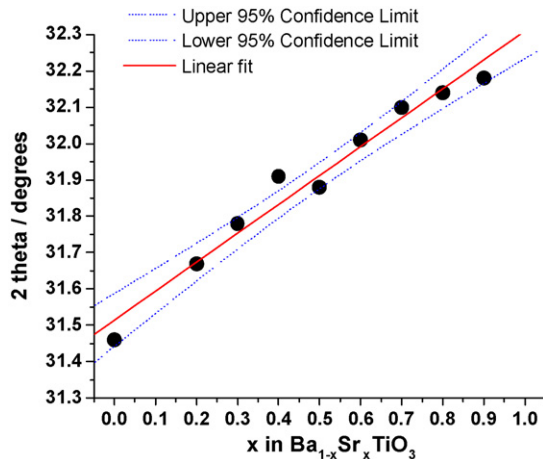

Fig. 7. Plot of variation in XRD 100% peak position vs. x for $Ba_{1-x}Sr_xTiO_3$ array (both $x = 0.1$ and 1 were missing from this array).

4. Conclusions

The LUSI robot was demonstrated to be able to automatically print and sinter libraries of bulk ceramic $Ba_{1-x}Sr_xTiO_3$ (BST), for $x = 0$–1 in steps of 0.1. The samples were prepared from suspensions of $BaTiO_3$ and $SrTiO_3$ nanopowders, stabilised with 1.2 wt% dispersant, and printed as arrays of 22 2 mm diameter dots, two of each composition, on alumina substrates. These were then sintered for 1 h at 1350 and 1400 °C by LUSI. EDXA and XRD confirmed the compositional gradient throughout the libraries, and SEM showed the samples to be well sintered, with a large 20 µm grain size for pure $BaTiO_3$ decreasing rapidly for increasing x values. The next step will be to investigate more complex perovskite ($[A][B]O_3$) libraries, such as $[(M^{2+})_{1-a}(M^+_{1/2}M^{3+}_{1/2})_a][(M^{4+})_{1-b-c}(M^{5+}_{2/3}M^{2+}_{1/3})_b (M^{3+}_{2/3}M^{6+}_{1/3})_c]O_3$, over a range of compositions and sintering temperatures.

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