

High throughput experimentation for the development of new piezoelectric ceramics

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Abstract Piezoelectric ceramics based on the perovskite $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) system are widely used as sensors and actuators. The toxicity of lead has motivated research in the field of alternative environmentally friendly lead-free materials. Lead-free piezoelectric ceramics are numerous and in comparison to PZT poorly investigated. The performance of PZT cannot yet be achieved by any lead-free material. Thus High Throughput Experimentation (HTE) shall be applied to discover new lead-free piezoelectric ceramics. In the present study a parallel solid state synthesis method was established for bulk ceramics. Libraries consisting of chemically diverse oxides are produced via the mixed-oxide route. Subsequently, classical piezoelectric parameters such as ϵ , d_{33} and Curie temperature are screened. The high throughput route, which allows the synthesis and characterisation of over one hundred samples per week, has to be validated with PZT samples. The morphotropic phase boundary was clearly identified and dielectric measurement shows excellent results. The method may be extended to lead-free materials.

Keywords HTE · Piezoelectric ceramics · Reactive sintering · PZT

1 Introduction

State-of-the-art piezoelectric materials are lead-based PZT materials. Due to the high toxicity of lead oxide, these

materials must be replaced by environmentally friendly (lead-free) materials. Lead-free piezoelectric ceramics with perovskite structure to replace PZT-based materials are numerous [1] but have been poorly investigated [2]. Conventional investigation of these new materials is too slow to meet the requirements of fast developing markets. High Throughput Experimentation (HTE) techniques are increasingly used for the discovery of new materials such as catalysts, polymers or electronics materials [3]. Often thin film technologies producing high sample throughput are applied to generate material libraries [4]. Thin film arrays are of limited value for piezoelectric ceramics, since important properties such as d_{33} as a function of grain size, doping and processing can only be determined through the analysis of bulk samples. The development of bulk ceramics, however, requires time-consuming synthesis and characterisation. Thus, new methods have to be developed to speed up the screening of ceramics with preparation methods similar to classical methods. The challenge of this work is to find a compromise between sample throughput and quality.

HTE as well as combinatorial synthesis should be applied to discover and optimise new lead-free piezoelectric ceramics. Before the screening of lead-free piezoelectric ceramics can start, HTE methods have to be established and validated with standard PZT.

2 Experimental

2.1 Processing

Conventionally an amount of approximately 300 g (1 mole) is required to investigate a new material composition and ceramic samples of 2 g are manufactured. This amount of material allows sensitive parameters such as calcination and

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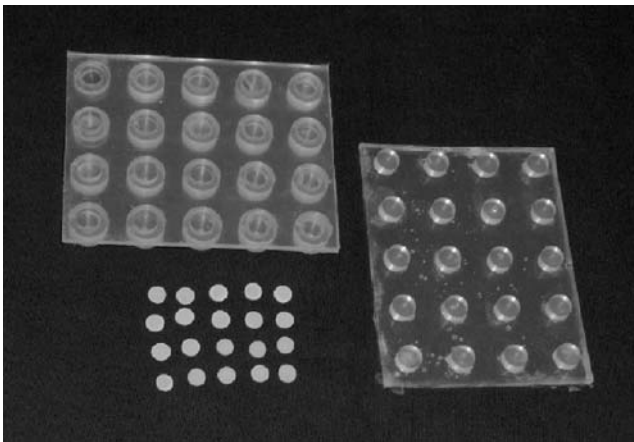


Fig. 1 Silicone moulds for the isostatic pressing of ceramic samples

sintering temperatures to be adjusted, as well as allowing complete characterisation of the material. To achieve higher sample throughput, the mass for each ceramic sample was reduced to 0.5 g per sample (samples dimensions: ~7 mm in diameter and 1 mm in thickness). However, since the processing parameters have a strong influence on the properties of the samples, these need to be screened as well as the compositions. Five samples are required for reliable characterisation. Thus to allow four processing parameters to be screened, 20 samples are needed. For each composition a total mass of 15 g was prepared.

The weighing of powder had initially been carried out with a pipetting robot but as the quantity of powder is quite high automated powder dosing is not suitable. Consequently dosing is carried out manually. After dosing, the powders are ball-milled in water or in alcohol for three hours in a planetary ball mill at high speed. For 15 g small containers can be used; this allows simultaneous milling of eight containers. Afterwards the slurries are dried overnight in a freeze dryer. Then the powders are used to fill the wells of a specially designed silicone mould (Fig. 1). The moulds

Table 1 Comparison of the two methods.

HTE method	Time
Dosage of 8x0.1 mole	2h
Grinding in planetary ball-milling machine	3h
Drying in freeze dryer	24h
Moulding in isostatic press (160 samples)	2h
Reactive sintering	24h
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Conventional method	Time
Dosage of one mole	0,5h
First grinding and drying	36h
Calcination	10h
Second grinding and drying	36h
Granulation	2h
Moulding in uniaxial press (40 samples)	1h
Sintering	24h

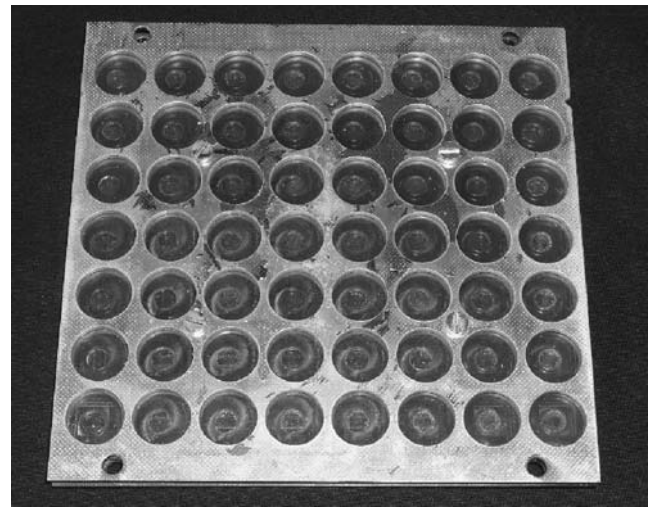


Fig. 2 8×7 silicone matrix in a metal mask as sample holder for silver deposition

were designed to allow parallel isostatic pressing. The green samples (20/composition) are reactively sintered under different conditions (five samples of one composition are stacked in an alumina boat).

The reactive sintering is a simple and time-saving processing method, in which the oxide mixtures are directly sintered at a high temperature without undergoing a calcination step. The reactively sintered samples are generally not as dense as conventionally prepared samples. The density, however, affects the properties of the material drastically. To ensure a higher density of the ceramic samples the green density of the sample must be as high as possible. Higher pressure means higher green density, which thus leads to higher density of the sintered samples. To obtain a density for reactively sintered samples comparable to the density of the conventionally sintered samples, the green pellets have to be pressed at high pressure; there-

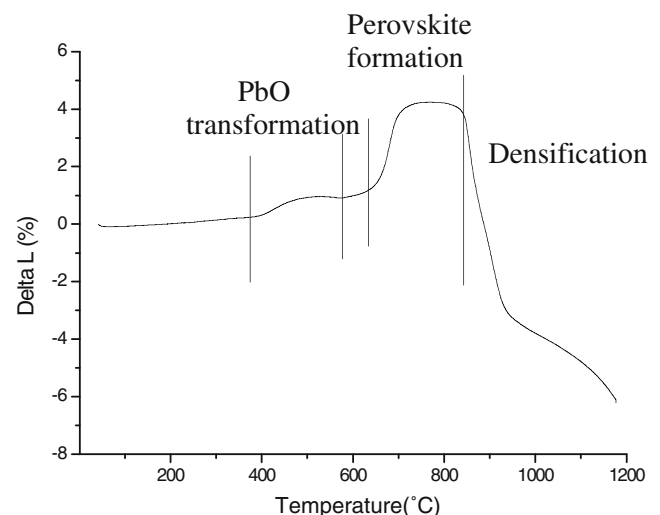


Fig. 3 Dilatometer measurement showing the sintering behaviour of a reactively sintered PZT

Table 2 Density of different samples.

Sample	Density [g/cm^3]
Conventionally manufactured	7.7939
Reactively sintered	7.4697
Reactively sintered + dwell at 750 °C for 2 h	7.4942
Reactively sintered + dwell at 850 °C for 2 h	7.5273

fore samples were isostatically pressed up to 2,500 bar at room temperature. In order to enhance densification and homogeneity an additional dwelling is realised at the calcination temperature (generally between 700 and 850 °C) for 2 h.

After reactive sintering the samples are planar polished and prepared for characterisation.

Table 1 compares both methods. The HTE method as described can improve the development of the materials by a factor of up to four. The steps and times for the HTE method are given for eight compositions worked on in parallel. The time for the conventional method is given for one composition; parallel working is difficult.

An alternative calcination step can be inserted to enhance the quality of the ceramic.

The powders are manually weighed in plastic cups. A solvent is then added to the cup and mixed together with the powder in a Speed Mixer DAC 150 FVZ. The solvent is evaporated in a drying furnace. The powders are then calcined in alumina crucibles at 750 °C for 2 h. The

powders obtained are ball-milled in water or in alcohol. The next steps are carried out as described above.

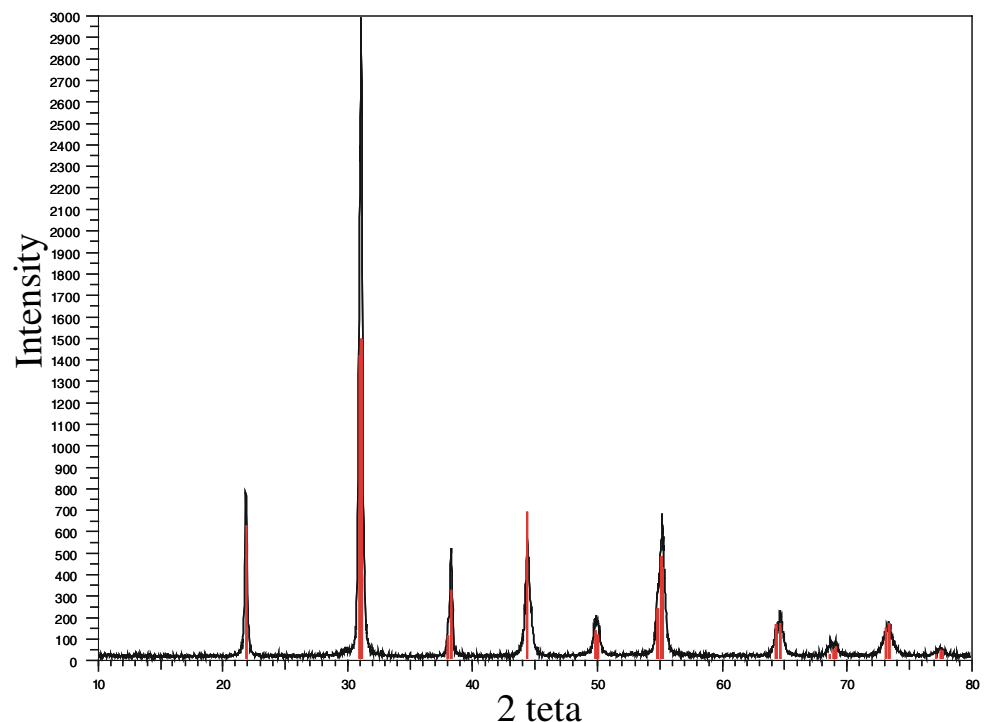
2.2 Characterisation

For characterisation the samples need electrodes on both faces. To provide reliable displacement values the entire surface of the ceramic needs to be covered by an electrode.

After sintering and planar polishing the samples are sputtered with a silver film applied via vapour deposition. Due to the variation in the composition and sample preparation, there is some variation in the diameters of the prepared samples. A silicone matrix as shown in Fig. 2 was developed to allow the clamping of such samples. The silicone is flexible, and thus adapts perfectly to slight diameter variations of the samples. The chosen mask allows the vapour deposition of silver on 56 samples at the same time. The operation has to be carried out on both sides. Special attention is paid to the edge of the samples. They must be free of silver in order to avoid short circuits.

The complete characterisation of a sample begins with the determination of the permittivity before poling measured with a Wayne Kerr Automatic Precision Bridge B905. Then the samples are poled and the permittivity is measured again. The d_{33} values are measured with an individually-designed set-up. The samples are placed between two tips where the displacement and the voltage can be recorded. The displacements are measured with a Feinpruef Millitron 1204 IC and the voltage is applied via a

Fig. 4 X-ray diffraction pattern of reactively sintered PZT with 2% Nd



Fug bipolar high voltage source. The samples were measured five times, three up to 2 kV/mm and two up to 1 kV/mm. The piezoelectric data were obtained using standard methods [5].

3 Results

3.1 X-ray diffraction and microstructure

The reactive sintering of PZT-based piezoelectric ceramics has been previously investigated [6]. However, PZT-based ceramics were difficult to process via this method, because large amount of PbO excess were needed to induce a liquid phase sintering.

As a test system PZT with 2% Nd was selected. First a dilatometer measurement was carried out with an auto-ranging Keithley multimeter (see Fig. 3). The reactively sintered material shows a first anomaly between 400 and 550 °C. This hump is the sign of the transformation of PbO

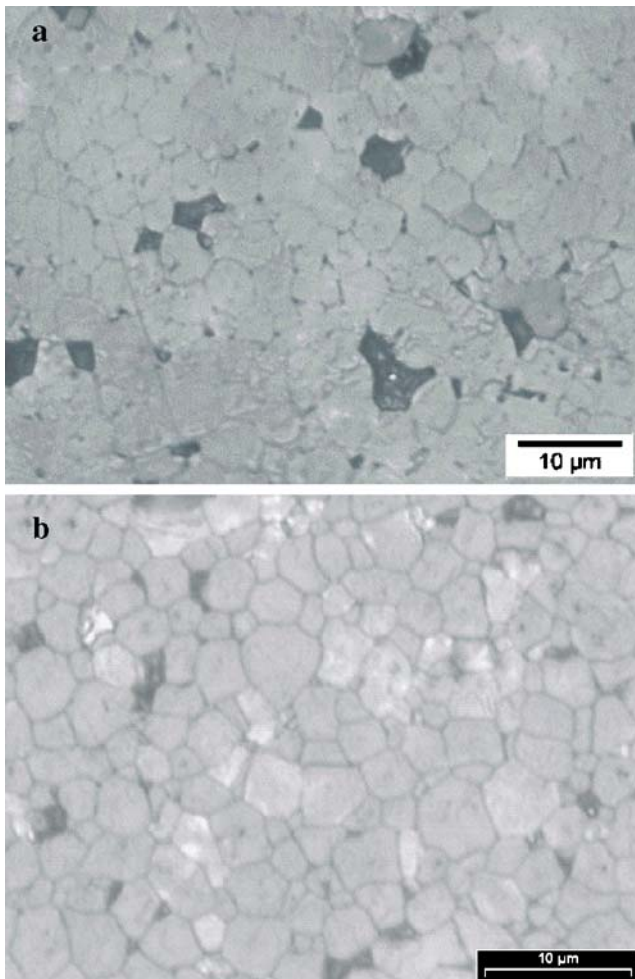


Fig. 5 Light microscope image of PZT reactively sintered (a) and conventionally sintered (b)

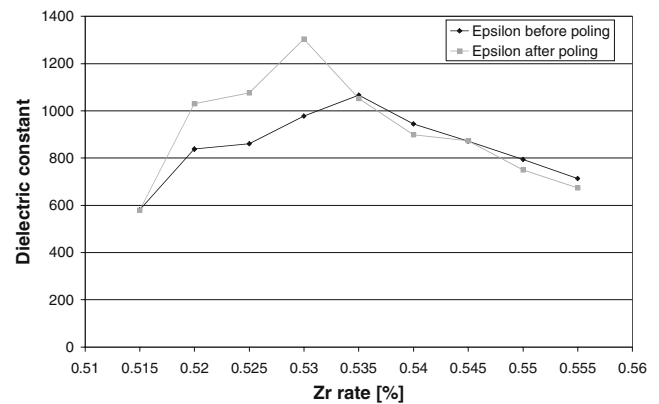


Fig. 6 Dielectric constants of reactive-sintered PZT samples

into Pb_3O_4 [7]. Then the perovskite is formed between 750 and 900 °C and the material densifies with a linear shrinkage of 11%.

The densities of the samples were measured with a Micrometrics AccuPyc 1330 helium picnometer. The values of Table 2 show that the densities of reactively sintered samples are 95% of the density of conventionally manufactured samples. A dwell at 850 °C for 2 h provides an enhancement of the densification and the density rises to 97% of the density of conventionally manufactured samples.

To control the phase formation, an XRD pattern was carried out on one sample. As shown in Fig. 4 the material obtained shows a pure perovskite phase.

The surfaces of polished and etched reactively and conventionally sintered samples were observed under a light microscope (Fig. 5a and b). As shown in Fig. 5 the average grain size of the reactively sintered sample is 5 µm and the grain size of the conventionally sintered sample is 3.5 µm. The microstructure of the reactively sintered sample shows a high closed porosity with large channels.

3.2 Dielectric characterisation

Samples were produced with a variation in the zirconium/titanium content between 51 and 55% Zr with 0.5% steps. The dielectric values of the HTE samples with $\epsilon=923$ and $\tan \delta=2.3\%$ for a zirconium rate of 53% were already nearly as good as the values of conventionally manufactured samples with $\epsilon=1,042$ and $\tan \delta=1.4\%$ [8]. The morphotropic phase boundary is clearly identified. Figure 6 shows the values of the permittivity before and after the poling for reactively sintered samples with a dwell at 800 °C for 2 h. The same tendency is observable in each curve: a peak in the area of 53% Zr. The MPB is clearly identifiable for the samples which contain between 52 and 53.5% zirconium because the permittivity after poling is higher than the permittivity before poling.

Figure 7 shows the difference between the dielectric constant before and after poling for four different zirconium

rates. The grey columns are the compositions with 3% Pb excess and the stroked out columns are those with 5% Pb excess. The brighter colours show a reactive sintering without dwelling at calcination temperature; the darker colours show a dwell at different calcination temperatures (the darker the colours are, the higher the dwell temperature). This figure shows the importance of PbO excess during the processing of PZT materials as well as the dwelling time during the calcination step. PbO excess and control of the atmosphere are two important parameters for classic sintering of ceramics and particularly for PZT [9]. The PbO excess must be present to induce the liquid phase during sintering which allows higher densities to be reached. PbO vaporisation was controlled during sintering through the use of a firing boat which was saturated with a mix of PbO and ZrO₂ before. The optimal parameters found are an excess of 3% of PbO and a dwelling at 850 °C for 2 h. The optimal excess of PbO was shown not to be as high as in previous reports [10]. The dwelling at 850 °C is optimal because calcination takes place between 700 and 875 °C. The temperature is chosen at the end of the calcination step when diffusion is fast but densification does not begin. At lower temperatures (<800 °C) the formation of the perovskite could not have been totally completed and higher temperatures showed no benefit either. As has been stated [11], the presence of PbO excess is crucial in achieving high density PZT. On the other hand, too large amount of PbO excess endangers good densification due to the rapid formation of a liquid phase followed by a rapid particle rearrangement, and solution/precipitation induces an inhomogeneous microstructure with large pores [9]. This may partly explain the optimal PbO excess being 3%.

Figure 8 shows the piezoelectric coefficient d_{33} of samples with different preparation conditions for the same range of compositions. The bright grey line shows the results of the conventionally prepared samples. The dark

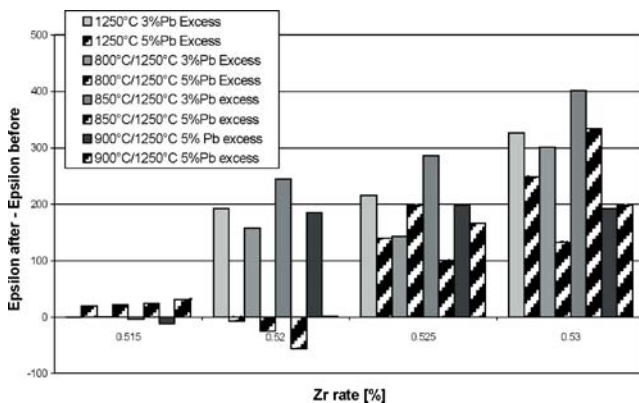


Fig. 7 Relative permittivity before and after poling of different PZT samples with zirconium rate variation. The temperatures indicated are dwelling temperature/sintering temperature

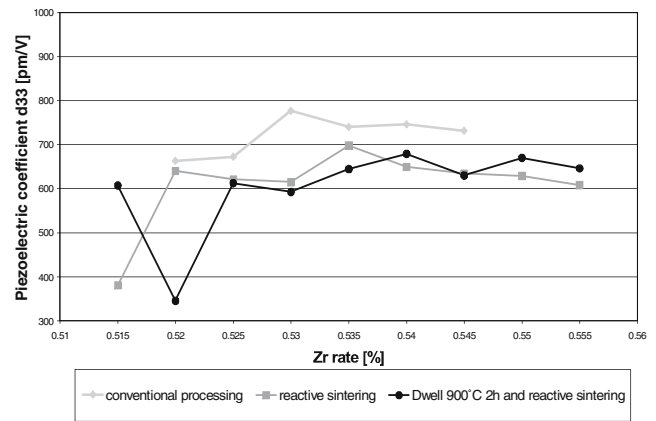


Fig. 8 Piezoelectric coefficient in poling direction (d_{33}) at 2 kV/mm

grey and the black lines are the values of the reactively sintered samples; the black line represents values of samples with a dwell during the sintering at 900 °C for 2 h. All the samples contained 3% PbO excess and were sintered at 1,250 °C for 2 h. The d_{33} values of the reactively sintered samples are lower than the values of the samples conventionally sintered. This is an expected result due to the lack of density of the samples; nevertheless the values are already close to the conventionally sintered ones and it should be noted that in the morphotropic phase boundary the values are somewhat higher (Zr rate 0.53–0.535).

The values of the samples having suffered a dwell at 900 °C are lower. This dwell, being in the densification zone, impairs the perovskite formation and the ceramic shrinks without having formed the perovskite.

4 Discussion & conclusion

In this study, a solid state synthesis and characterisation method for piezoelectric ceramics was established. The method not only allows the quick screening of different material compositions but also the screening of different processing parameters. The throughput of the method is eight compositions per week, which means that an increase in production by about four times relative to the conventional production is achieved. However, the throughput is significantly lower than the throughput of generally applied combinatorial thin film methods. Nevertheless, for the development of new ceramics it is more favourable and straightforward to screen ceramic samples. Crucial parameters such as calcination and sintering behaviour, and the influence of doping elements can all be screened on the final ceramic prototype. Thus, a combination of thin film technology with its high sample throughput and this new method might achieve best results for materials development: interesting areas of materials can be identified by thin film technology, and adaptation to ceramics shall be carried

out with the solid state method including optimisation of composition and processing as well as the choice of doping elements. With the established method, ceramic samples of remarkably high quality are produced in parallel which allows the precise characterisation of all properties of interest, i.e. permittivity, piezoelectric coefficient and Curie temperature.

For PZT, this method achieved excellent results. The MPB is clearly observable through the values of permittivity before and after poling as well as the values of the piezoelectric coefficient d_{33} . In both electric measurements, i.e. permittivity and piezoelectric coefficient, the values of the reactively sintered samples are almost as high as the values of the samples manufactured by conventional methods.

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