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Tape casting of ferroelectric, dielectric, piezoelectric and ferromagnetic materials

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Abstract

Tape casting is a feasible method for preparing ceramic tapes with different electrical and magnetic properties for multilayer ceramic devices. This paper describes the tape casting process for several different electroceramic materials (BST, PZT, NZF and ZSB) utilising similar organic additive and solvent systems. The properties of tapes with different ceramic compositions before and after sintering are investigated, including surface roughness, shrinkage and microstructures. The parameters affecting the casting, shrinkage, lamination, thickness and tensile strength of green tape are also presented. This enables process design for tape which can be used in devices with true integration of dielectric and piezoelectric, ferroelectric and ferromagnetic layers in 3-dimensional multilayer structures.

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1. Introduction

Tape casting has been widely used in electronics industry for capacitors, piezoelectric and electrostrictive devices, ferromagnetic memories, ceramic substrates, fuel cells and catalytic substrates.[1,2] This process offers the widest thickness range and the thinnest self-supporting layers. Additionally, it has no fundamental restrictions concerning the use of solvent/binder systems, and it can be set up either as a continuous process to manufacture large quantities of smooth tapes or as a small discontinuous laboratory route for cost-effective testing applications. Nowadays, green tapes are printed with conductors, punched for holes, laminated and co-fired to manufacture multilayer devices. However, the components and applications introduced are generally composed of layers prepared from the same electroceramic powder such as dielectric or piezoelectric materials, and only a few studies investigating the preparation of components with different types of electroceramic layers have been reported. Furthermore, these structures are typically composed at high sintering temperatures, as reported by McNulty et al., for instance, with lamination and co-firing of $BaTiO_3$, $(Ni,Zn)Fe_2O_4$ and Al_2O_3 based tapes.[3] In more advanced integration, the use of ferromagnetic, dielectric, ferroelectric and piezoelectric layers with high conductive silver pastes in low temperature co-fired ceramic (LTCC) applications (<1000 °C) would improve the diversity and performance of components with low production costs.

The main problem of having different electroceramic tapes in one multilayer component is their unequal optimal sintering temperatures (850–900 °C), but even when this question is not taken into account, the process aspect prior to sintering should be solved. The main target of this work is to demonstrate that similar organics can be used for very different electroceramic powders in tape casting, regardless of the size or surface condition of powder particles. This is an important aspect, because lamination is more successful if the organic additive systems of the different ceramic layers are equal. Furthermore, this enables convenient adjustment of lamination parameters, including pressure or temperature, for multimaterial components.

This paper describes the tape casting process for several different electroceramics (ferroelectric, piezoelectric,

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ferromagnetic and dielectric) utilising similar organic additive and solvent systems. The composition of barium strontium titanate (BST) used in this work is $Ba_{0.7}Sr_{0.3}TiO_3$. It is a widely known ferroelectric material used in capacitors, phase shifters and tuneable filters.[4,5] Lead zirconate titanate (PZT) is a piezoelectric ceramic used e.g. in actuators, sensors, buzzers and transformers.[6] The ferromagnetic material is $Ni_{0.55}$-$Zn_{0.5}Fe_{1.85}O_x$ (NZF), which is a common material in magnetic cores. The ZSB, which contains $MgTiO_3$–$CaTiO_3$–ZnO–SiO_2–B_2O_3, is a dielectric LTCC material for multilayer capacitors, resonators and filters.[7] The tape properties for each ceramic composition before and after sintering are investigated, including their surface roughness, tensile strength, shrinkage and microstructures. Additionally, the casting, lamination and sintering parameters are presented.

2. Experimental procedure

The barium strontium titanate (BST) powder was supplied by Fuji Titanium Industry Co. Ltd, Japan, and the lead zirconate titanate (PZT) powder by Ferroperm, Denmark, with Type PZ26. The NZF powder, $Ni_{0.55}Zn_{0.5}Fe_{1.85}O_x$, was prepared by the oxide mixing method. The ZSB powder was made of high sintering temperature (1360 °C) dielectric, $MgTiO_3$–$CaTiO_3$ (Fuji Titanium Industry Co. Ltd., Japan), and calcined ZnO–SiO_2–B_2O_3.[7] All pure oxides were supplied by Johnson Matthey GmbH, Germany. The specific surface areas (SSA) of all powders for tape casting were measured with a BET analyser (OmniSorp 360CX, Coulter Electronics Inc., Ltd., Luton, UK). The particle size distribution was measured by Malvern Mastersizer (MS1002, Malvern Instruments Ltd., Malvern, UK).

The powders were first mixed with solvents and dispersant in a ball mill for 24 h, then plasticizers and binder were added and mixing for another 24 h to obtain the slurry. The slurry system was the same for all the four powders. The solvents were ethanol and xylene. The dispersant was Blown Z-3 menhaden fish oil, which also acts as surfactant. The binder itself was polyvinyl butyral (B98), and the compatible plasticizers were butyl benzyl phthalate (S160) and polyalkylene glycol (Ucon). Organic additives, all commonly used in tape casting, were supplied by Richard E. Mistler, Inc., USA. The tape casting was done with a laboratory caster (Unicaster 2000, University of Leeds, Leeds, UK).

In all cases, the amounts of additives and solvents were varied, starting from the amounts presented by Mistler and Twiname,[2] until a castable slurry producing high-density (higher than 50% compared to the sintered values) green tapes was obtained. Additionally, the tapes were required to be flexible and strong enough to stand subsequent process steps, such as handling, punching and lamination, without cracking or warping. The tensile strengths of green tapes were measured with an Instron 5544 testing system (Instron Company, UK) and their surface roughness in the green and sintered stages with Dektak^{3}ST (Sloan Technology, Santa Barbara, CA, USA). Densities were evaluated from dimensions and weight and shrinkage from dimensional changes. The microstructures were studied with SEM (Jeol JEM-6400, Tokyo, Japan) and porosities were evaluated by Soft Image System (Gmbh, Munster, Germany) and line analysis.

3. Results and discussion

It is essential that the starting powders are well characterised before the tape casting process. Parameters such as the particle size and distribution, specific surface area (SSA), purity and powder density are defined. Generally, powders with SSA 1–15 m^2/g are suit for the tape casting process.[2] The measured SSA values of our starting powders, BST, PZT, NZF and ZSB, were 3.0, 1.0, 4.9 and 2.6 m^2/g respectively. All these powders had SSA values suitable for the tape casting process. The mean particle size of the BST, PZT, NZF and ZSB powders were 1.2, 3.6, 0.5 and 1.8 μm respectively.

Taking into account of the general requirements of the tape manufacturing process[2] along with the demands for density, strength and flexibility mentioned earlier, the appropriate amounts of additives and solvents for each powder were found to be as presented in Table 1. It must be kept in mind that the slurry compositions shown in Table 1 are mainly tentative and cannot be claimed to be the absolute optima, since so many components could be varied to meet many vaguely defined demands. However, it was noticed that, in a very early stage of the slurry and casting tests, the ZSB powder required more solvents than the others, although no extra amount of additives was needed, and its large value of SSA should have predicted opposite behaviour. The PZT powder, on the other hand, required the highest amount of binder with the lowest amount of solvents. This could be explained by the different surface conditions of the powder particles.[1]

The physical properties of the green tapes are shown in Table 2 and their microstructures in Fig. 1. In the

Table 1
Slurry compositions for different electroceramic powders (wt.%)

	Powder	Ethanol	Xylene	Fish oil	B98	S160	Ucon
BST	60.0	16.5	16.5	1.2	3.8	1.0	1.0
PZT	62.6	11.7	17.6	0.9	4.8	1.2	1.2
NZF	60.0	16.1	16.1	1.2	4.4	2.2	0
ZSB	55.8	18.5	18.5	1.1	4.1	1.0	1.0

green state, the average particle sizes of BST and PZT (Fig. 1a and b) were around 1 and 0.3 μm for NZF powder (Fig. 1c). The observed average particle size differences between the powders and the green state tapes confirmed the existence of agglomerates present in original powders. The microstructures of the green tapes were uniform. The ZSB contained some very large particles (> 5 μm), probably due to calcination (Fig. 1d). This can also be seen in the average surface roughness (RA), which is by far the most commonly used parameter in surface finish measurements. Graphically, RA is the area between the roughness profile and its centre line divided by evaluation length. A RA value of 0.2 μm was measured for the first three tapes and 0.5 μm for the ZSB.

The green densities of all tapes were high. The lowest value compared to the sintered was measured for the ZSB tapes (57%), but it was still far from the lowest required level (50%). The main reason for the lowest density in this case might be the large amount of solvents needed. On the other hand, the green tape made of NZF had very high density (78% compared to the sintered value), although only average amounts of solvents and binders were required. This tape also showed the highest tensile strength (4.6 MPa), and thus it cannot be said that the relative green density or tensile strength have straightforward correlations with the amount of binder or solvents. In the case of ZSB powder, a larger amount of binder would naturally have produced stronger tape but at the expense of green density. Furthermore, it has been earlier determined that its strength is high enough to stand the subsequent multilayer preparation steps.[7]

Table 2
Properties of different green tapes

	RA (μm)	Tensile strength (MPa)	Density (Mg/m^3)
BST	0.2	3.8	3.5
PZT	0.2	4.1	4.2
NZF	0.2	4.6	3.4
ZSB	0.5	1.2	2.1

The motivation for the production of multilayered ceramic devices is the ability to laminate several layers of green tape together to produce a structure that sinters together into a monolithic solid ceramic part. Three basic parameters in lamination (temperature, pressure and time) must be controlled. The temperature depends basically on the type and amount of plasticizers and binder in the slurry. The dwell time of lamination must be sufficient to heat the entire stack, and the number of

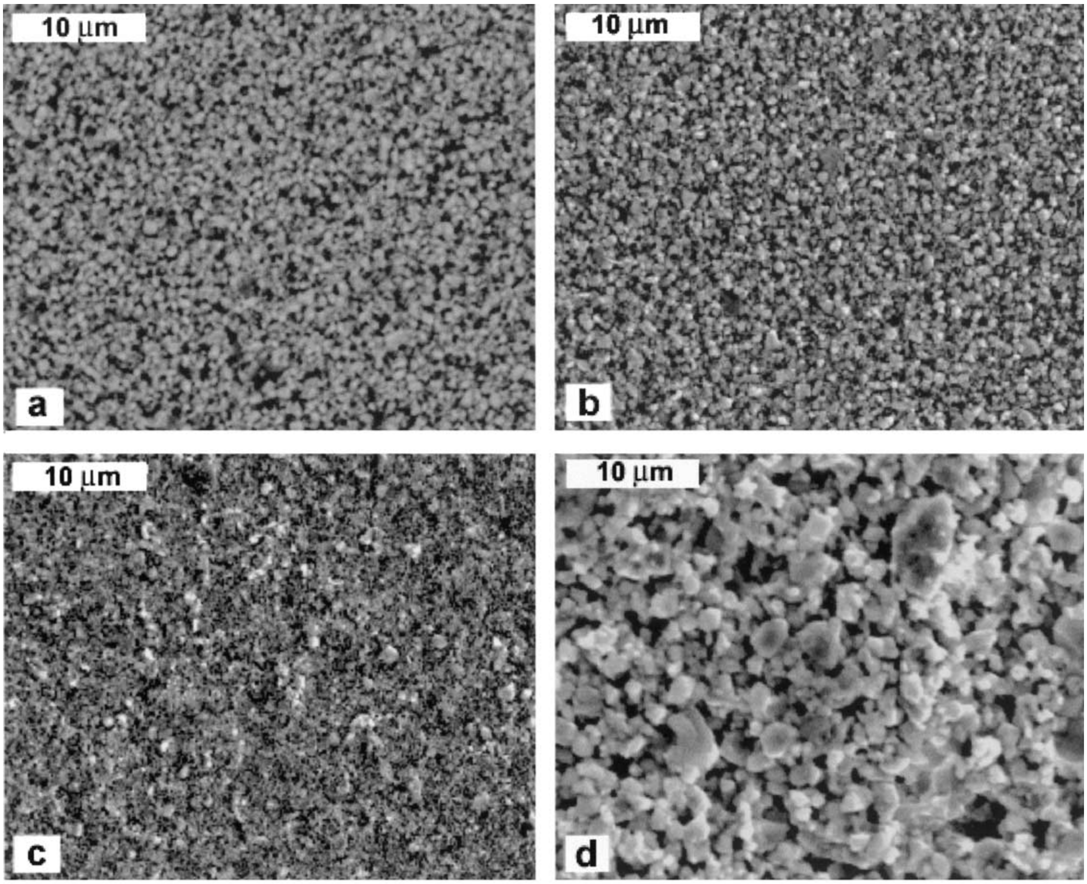

Fig. 1. SEM images of (a) BST, (b) PZT, (c) NZF and (d) ZSB green tapes.

layers or overall thickness should also be considered. Sufficient pressure must be applied to provide intimate contact between the layers without distorting the laminated part.[1] In our study, for 10–20 layers of green tape the lamination temperature was 70 °C, pressure 15–20 MPa and dwell time 15–20 min. Sintering of the PZT and BST tapes was done as recommended by the powder manufacturer. For self-prepared powders, sintering temperatures tested to be optimal from the microstructural point of view for bulk samples were used (Table 3).

Table 3
Properties of different sintered tapes

	Sintering temperature (°C)	RA (μm)	Shrinkage X,Y/Z (%)	Density (mg/m^3)
BST	1300	0.2	15.1/17.4	5.1
PZT	1050	0.2	18.7/18.6	7.1
NZF	1300	0.5	14.8/10.5	4.5
ZSB	900	0.6	17.8/19.0	3.7

The roughness, shrinkage and density of different sintered samples are shown in Table 3 and their microstructures in Fig. 2. The surface of sintered BST and PZT remained very smooth with RA values of 0.2 μm, but NZF showed coarsening, which can also be seen from the SEM image (Fig. 2 c). The microstructure of ZSB (Fig. 2d) was polyphased system, as we reported before.[7] The densities of all fired tapes were moderately close to the bulk samples, as also confirmed by SEM images showing low porosity. The porosity of sintered BST, PZT, NZF and ZSB was 2.3, 2.5, 5.7 and 0.6% respectively. The shrinkage values varied somewhat, but they did not directly correlate with the used amounts of solvents or additives. This was especially true of the PZT and ZSB tapes, in which shrinkage in all directions was almost the same despite differences in their slurry compositions. However, the shrinkage differences between different tapes are able to produce a maximum deviation of 4 mm in a 100 mm sample in the XY direction. This 4% difference in the shrinkage is not negligible but it is low enough to produce flat and uniform multimaterial modules especially if the lamination parameters are adjusted properly and the structure is stacked symmetrically in vertical direction. The mutual lamination is able to decrease this deviation.

A more difficult problem with mutual sintering of different tapes is caused by the large deviation in the

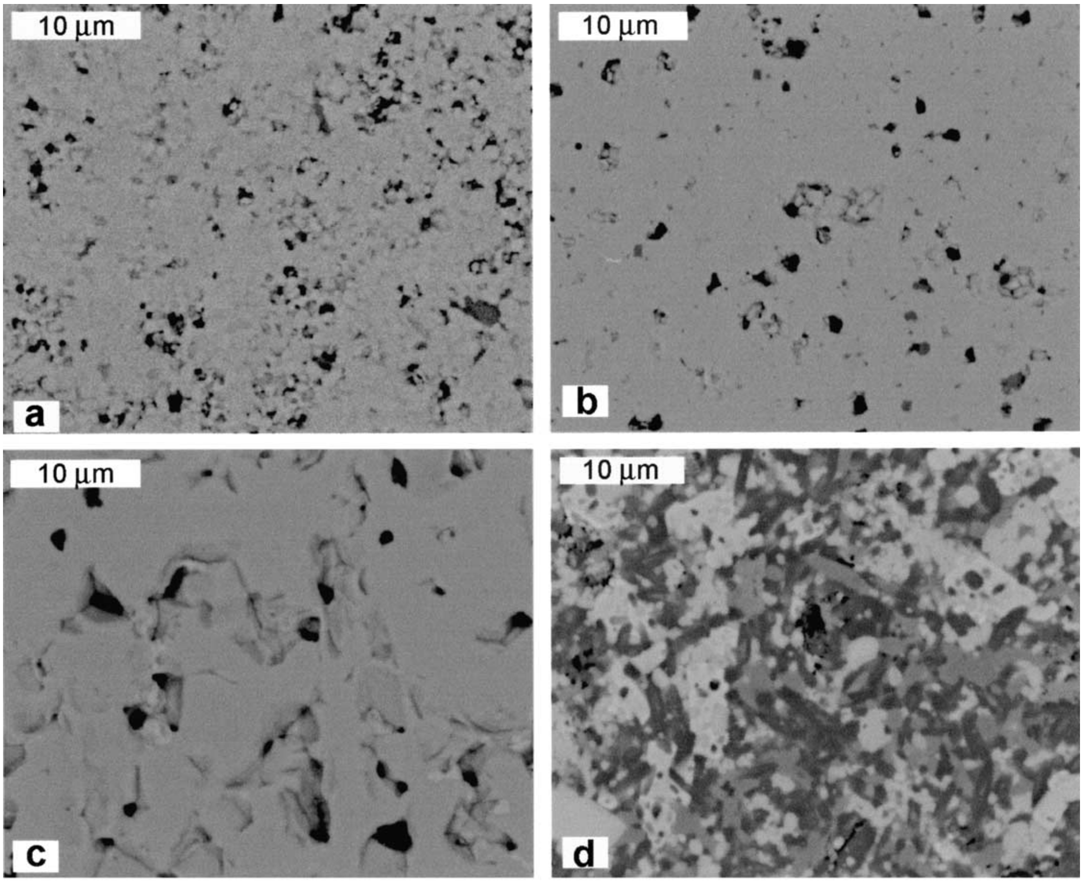

Fig. 2. SEM images of sintered tapes: (a) BST sintered at 1300 °C for 60 min, (b) PZT sintered at 1050 °C for 60 min, (c) NZF sintered at 1300 °C for 30 min and (d) ZSB sintered at 900 °C for 80 min.

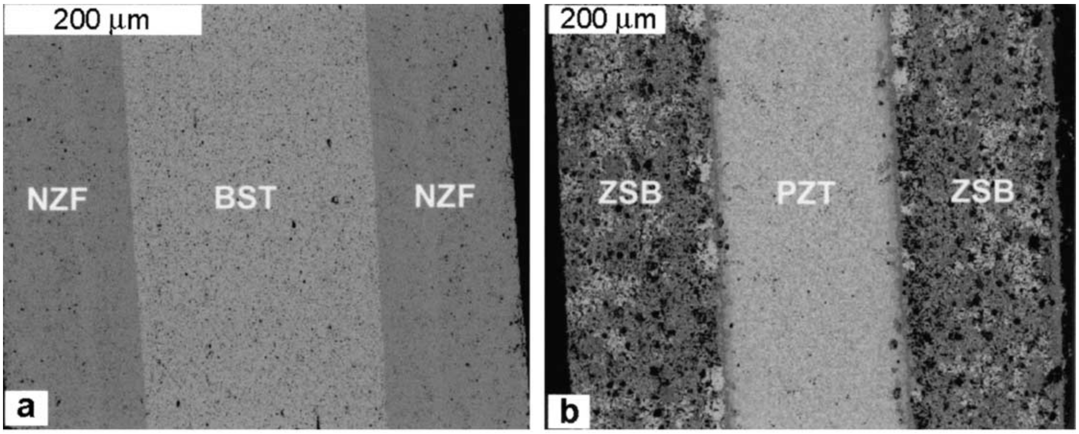

Fig. 3. SEM images of laminated and co-fired (a) BST and NZF (1300 °C, 60 min) and (b) PZT and ZSB (900 °C, 80 min) multilayer structures.

required sintering temperatures for each composition. This problem still requires lots of work, but two material combinations were tested here. Fig. 3a shows the cross-section of BST and NZF co-fired at 1300 °C for 60 min, and Fig. 3b shows the cross-section of ZSB and PZT sintered at 900 °C for 80 minutes. The interfaces of the different materials were clear without any delamination, showing that utilisation of the same slurry system really facilitates further processing. As there were some differences in shrinkage and density between BST and NZF, the co-fired ceramic multilayer showed some cracking and curling. However, further adjustment of slurry compositions can solve this problem. Another reason for cracking and curling might be their different thermal expansions.

In the case of a versatile multilayer component integrating all of these materials (BST, PZT, NZF and ZSB), the sintering temperatures of all compositions should be adjusted close to 900 °C. In fact, the dielectric portion of ZSB is already a result of this kind of work.[7] Similar work with BST has also been started.[5,8]

4. Conclusion

It was shown here that a similar slurry system can be used to prepare cast tapes from very different electroceramic powders (ferroelectric, piezoelectric, ferromagnetic and dielectric). All of the green tapes obtained had smooth surfaces (0.2–0.5 µm), high densities (>50% of sintered density) and at least moderate tensile strengths (1.2–4.6 MPa). After sintering, the tapes had moderately low porosity (0.6–2.5%), high density and good surface quality, although large grain growth and higher porosity (5.7%) could be observed in the NZF. The shrinkage values of different tapes differed to some extent, causing at maximum 4 mm difference in a 100 mm sample in the XY direction. This can be corrected with further adjustment of slurry composition, and mutual lamination of different tapes is also able to keep the deviation within acceptable limits. The laminated and co-fired multimaterial structures also showed that the utilization of the same additive systems in the tape casting procedure for each electroceramic composition produced good, well-defined interfaces between the different layers without delamination.

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