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BST powder with sol-gel process in tape casting and firing

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Abstract

Ferroelectric films such as Barium Strontium Titanate (BST) films are potential candidates for several microwave applications. In this work, the suitability of fine BST powder prepared by the sol-gel process for tape casting and firing were studied and compared with one commercial BST powder. The particle size of the sol-gel powder was 0.05–0.1 μm. The effects of different powders and slurry properties on the tape casting procedure, the thickness and tensile strength of the final tapes and their surface roughness were investigated. Furthermore, the sintering properties of different powders were measured using a dilatometer. The tapes made with sol-gel powder were sintered at 1250 °C and had large shrinkage.

Keywords: BST; Firing; Microstructure; Tape casting

1. Introduction

The tape casting process enables producing large, thin and flat ceramic layers which are self-supporting at different thickness generally from 0.025 to 1.27 mm.[1] Tape casting is an inexpensive continuous process for manufacturing large quantities of tapes. After screen printing of conductive patterns on the green tapes, the tapes can be laminated together by punching holes and co-fired to manufacture multilayer ceramic modules. Recently, ferroelectric films of Barium Strontium Titanates (BST) have been studied for tunable microwave devices, such as filters, antennas and phase shifters, because BST has high tenability, high permittivity and low loss.[2,3] The films are until now produced mainly by sputtering, CVD, spin coating, etc.[4,5] Integrating ferroelectric layers into multilayer ceramic modules with all layers prepared by tape casting would enable inexpensive mass production.

In this work, ultra-fine BST powder prepared by the sol-gel process for tape casting was studied, and the properties achieved were compared with a commercial BST powder. Because moderate tuning voltages are required, one target of this work was to prepare very thin BST tapes between 10 and 50 μm in thickness. Successful casting of such thin tapes depends mainly on the properties of the powder and the composition of the slurry. In this work, the particle size and specific surface area of the powders were studied first, but special attention was given to the slurry compositions for producing very thin but dense tapes of sufficient tensile strength to enable subsequent handling. The weight loss during sintering was also analyzed. Furthermore, shrinkage as a function of temperature and time was determined with a dilatometer using bulk samples, and the densification of laminated tapes was determined based on shrinkage and final density values. The average surface roughness of green tapes was also studied, because it is important for accurate printing of conductor patterns.

2. Experimental procedure

The sol-gel process used to prepare barium strontium titanate powders was described in our previous work.[6] The starting materials were $Ba(CH_3COO)_2$, $Sr(CH_3COO)_2$ and $Ti(OCH(CH_3)_2)_4$ with mole ratios of Ba:Sr:Ti = 0.7:0.3:1.0. Ultra-fine powder (BST-sg) was thus obtained after calcining the gel at 800 °C for 2 h. The $Ba_{0.7}Sr_{0.3}TiO_3$ powder prepared by the conventional oxide mixing method (BST-o) was supplied by Fuji Titanium Industry Co., Ltd, Tokyo, Japan.

Corresponding slurries were prepared with a ball mill. First, the powders were added to solvents and dispersants and mixed for 24 h, and then binder and

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Table 1
Slurry compositions (wt.%)

	Powder	Ethanol	Xylene	Fish oil	B98	S160	Ucon
BST-o	60.0	16.5	16.5	1.2	3.8	1.0	1.0
BST-sg	50.0	14.0	28.0	1.5	4.5	1.0	1.0

plasticizers were added to the mixture and mixing was continued for another 24 h. The compositions of the slurries are shown in Table 1. The solvents were ethanol and xylene, which are commonly used in the tape casting process. Menhaden fish oil is an effective dispersant that also acts as a surfactant as it contains lots of glycerol esters of saturated and unsaturated fatty acids. Blown Z-3 Menhaden fish oil was used in our experiments. The binder used was polyvinyl butyral (B98), and butyl benzyl phthalate (S160) and polyalkylene glycol (Ucon) were used as plasticizers. All these organic additives were supplied by Richard E. Mistler, Inc., Morrisville, USA. The casting was done by a laboratory caster Unicaster 2000 (University of Leeds, Leeds, UK) with a single doctor blade and 100–400 μm wide gaps. The tapes were shaped and laminated into multilayer at 70 °C, 15–20 MPa for 15–20 min, then firing at different temperatures. During the sintering the heating rate was 3 °C/min, but in the 200–600 °C range the heating rate was 1 °C/min in order to burn out the binder and other organics.

The specific surface areas (SSA) of the powders were measured by a BET analyzer COULTER OMNISORP 360CX (Coulter Electronics Inc., Luton, UK), and particle size and distribution were estimated by a transmission electron microscope TEM (Jeol JEM 100CXII, Tokyo, Japan). The surface roughness and tensile strength of the cast and dried green tapes were measured by Dektak^{3}ST (Sloan Technology, Santa Barbara, CA, USA) and Instron 8801 tensile strength testers (Instron Company, UK), respectively. The microstructures of the green tapes as well as the laminated and fired tapes were studied with a scanning electron microscope, SEM (Jeol JEM-6400, Tokyo, Japan). Shrinkage and weight loss were estimated from the dimensions and weights of laminated and fired tapes. Additionally, the powders with 2 wt.% PVA and 0.7 wt.% PEG were die-pressed into cylindrical pellets 25 mm in length and 10 mm in diameter, especially for dilatometric measurement (Orton Automatic Recording Dilatometer, Westerville, OH, USA) for investigating sintering behaviour.

3. Results and discussion

The specific surface area (SSA) of BST-sg was 18.7 m^2/g, which is sixfold compared to that of BST-o powder (3.0 m^2/g). BST-sg powder thus had high reactivity. TEM images of the powder (Fig. 1) clearly show that the particle size of BST-o was around 0.6–1.5 μm, while that of BST-sg was 0.05–0.1 μm. Furthermore, most particles of BST-sg powder had spherical shapes and limited distribution, while BST-o powder had a large size range of particles of irregular shape.

In the tape casting process, the important properties of the slurry are also notably affected by the organic additives used, such as the binder, plasticizers and dispersant. For example slurry viscosity should be carefully controlled because tape thickness decreases with decreasing the viscosity. Optimum viscosity values for tape casting slurries was 500–25,000 mPa s, according to R.W. Cahn.[7] In this case, it was especially important to

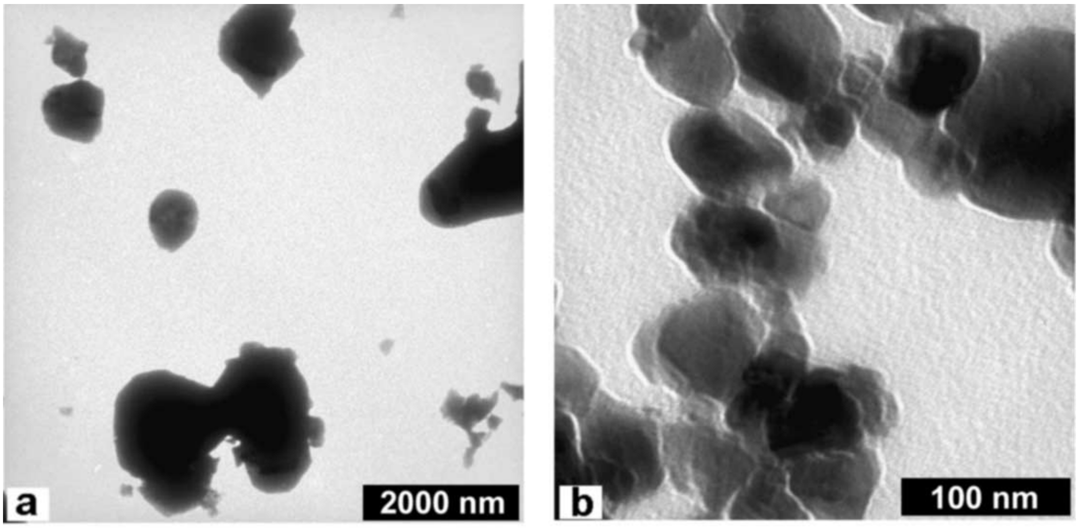

Fig. 1. TEM images of the studied powders of (a) BST-o and (b) BST-sg.

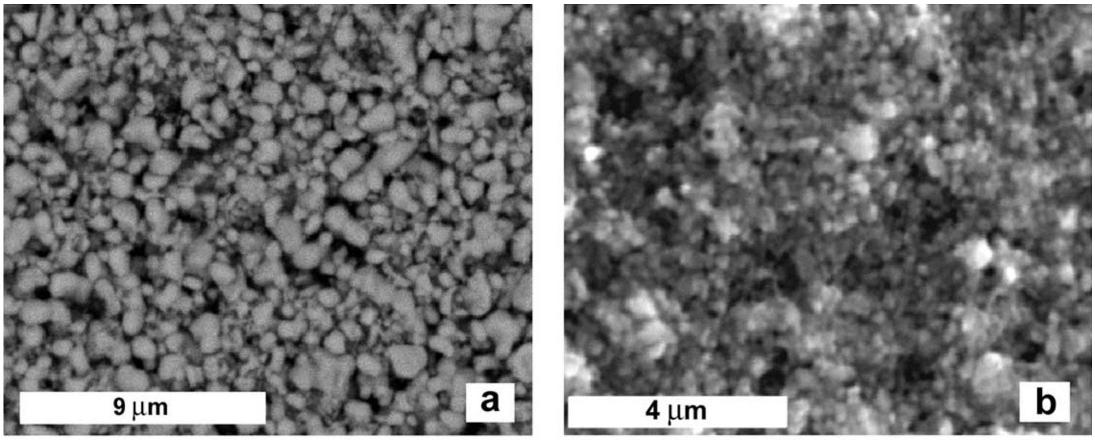

Fig. 2. Microstructures of green tapes of (a) BST-o and (b) BST-sg powders.

control the slurry properties, because the final target of the studies was to prepare very thin, self-supporting tapes (10–50 µm), which are most beneficial from the viewpoint of electrical tunability. The criterion for good slurry was the possibility to cast a thin and uniform tape. This was enabled by Newtonian type of viscosity.[8] Furthermore, high tensile strength and density of green tape were desirable qualities. The compositions of the slurries shown in Table 1 were chosen on that basis.

The mean tensile strength values of BST-o and BST-sg green tapes were 2.96 and 4.29 MPa, respectively. The tape made of sol-gel powder was stronger, which can be explained partly by the larger surface area of the powder and partly by the somewhat larger amount of binder needed. The surface roughness of BST-sg was 0.15 µm and that of BST-o 0.20 µm. The BST-sg tapes were smoother than BST-o, but the difference was not significant, though it was smaller in both cases than that reported for commercial ceramic tapes, 0.4 µm.[9]

Fig. 2 is the microstructures of corresponding green tapes, showing some agglomeration in the BST-sg tape. This can be explained by the large surface area and small particle size with larger surface energy, which causes more agglomerates, resulting in more difficulties in the preparation of good slurry. Generally, most powders fall within the SSA range of 1 to 50 m^2/g, with the vast majority of highly sinterable powders falling within 5–15 m^2/g. [1] It was obvious that more experiments are needed to modify the slurry composition for these ultra-fine powders.

Several layers of both green tapes were laminated at 70 °C and 15 MPa for 20 min and then sintered at different temperatures. Fig. 3 shows the microstructures of multilayer tapes made of BST-o and BST-sg and sintered at 1250, 1300 and 1350 °C for 1 h. The densities, shrinkage and weight losses of these samples are listed in Table 2.

After sintering at 1250 °C, both BST-o and BST-sg tapes had porous microstructures [Fig. 3(a) and (b)] with low measured densities of 3.9 and 3.8 Mg/m^3, respectively. However, the tapes made of BST-sg powder showed much more abundant shrinkage in all directions than the tapes made of BST-o powder. At the higher sintering temperature of 1300 °C, the shrinkage of BST-o in the X, Y and Z directions increased notably, but a further increase from 1300 to 1350 °C did not affect either shrinkage or density. The BST-sg multilayer, however, did not stand higher sintering temperatures than 1250 °C. These samples were blistered in the Z direction, and large pores were formed. This phenomenon might be due to over-firing and excessive carbons. Since the BST-sg powder was manufactured by the sol-gel process there might be some carbon atoms remaining in the structure. Furthermore, a smaller amount of additive which prevented delamination might be also one reason for this phenomenon. Fig. 3(f) shows that BST-sg had marked grain growth at higher temperatures and that grain size was more than 10 µm. The results indicate that, for tapes made of BST-o powder, a minimum sintering temperature of 1300 °C is required, which is far too high for tapes prepared from BST-sg

Table 2
Densities, shrinkage and weight losses of sintered tapes

	Sintering temperature (°C)	Density (Mg/m^3)	Weight loss (%)	Shrinkage X,Y (%)	Shrinkage Z (%)
BST-o	1250	3.9	11.3	6.8	9.1
	1300	5.1	11.4	14.7	13.0
	1350	5.2	11.4	15.1	13.0
BST-sg	1250	3.8	16.3	17.1	20.0
	1300	NA	16.8	25.3	NA
	1350	NA	24.6	35.7	NA

powder. In this case, a longer sintering time might have been better.

For further understanding of the sintering behaviour, dilatometric measurements were made. As before firing, the green densities of both multilayers laminated by green tapes and dry-pressed bulk compacts were very close to each other, compacted powders of BST-o and BST-sg were used for dilatometry. Shrinkage as a function of temperature and time was shown in Fig. 4(a) and (b).

The dilatometric curves of BST-o and BST-sg in Fig. 4(a) showed their similar shrinkage behaviour upon increasing temperature. This observation led to the conclusion that more work is needed to optimize the corresponding slurry composition.

A simple model was used to evaluate the experimental data. The relative change in length, $\Delta L/L_o$, proportional to the dwell time t, can be shown to follow Eq. (1),[10,11] where K is a constant.

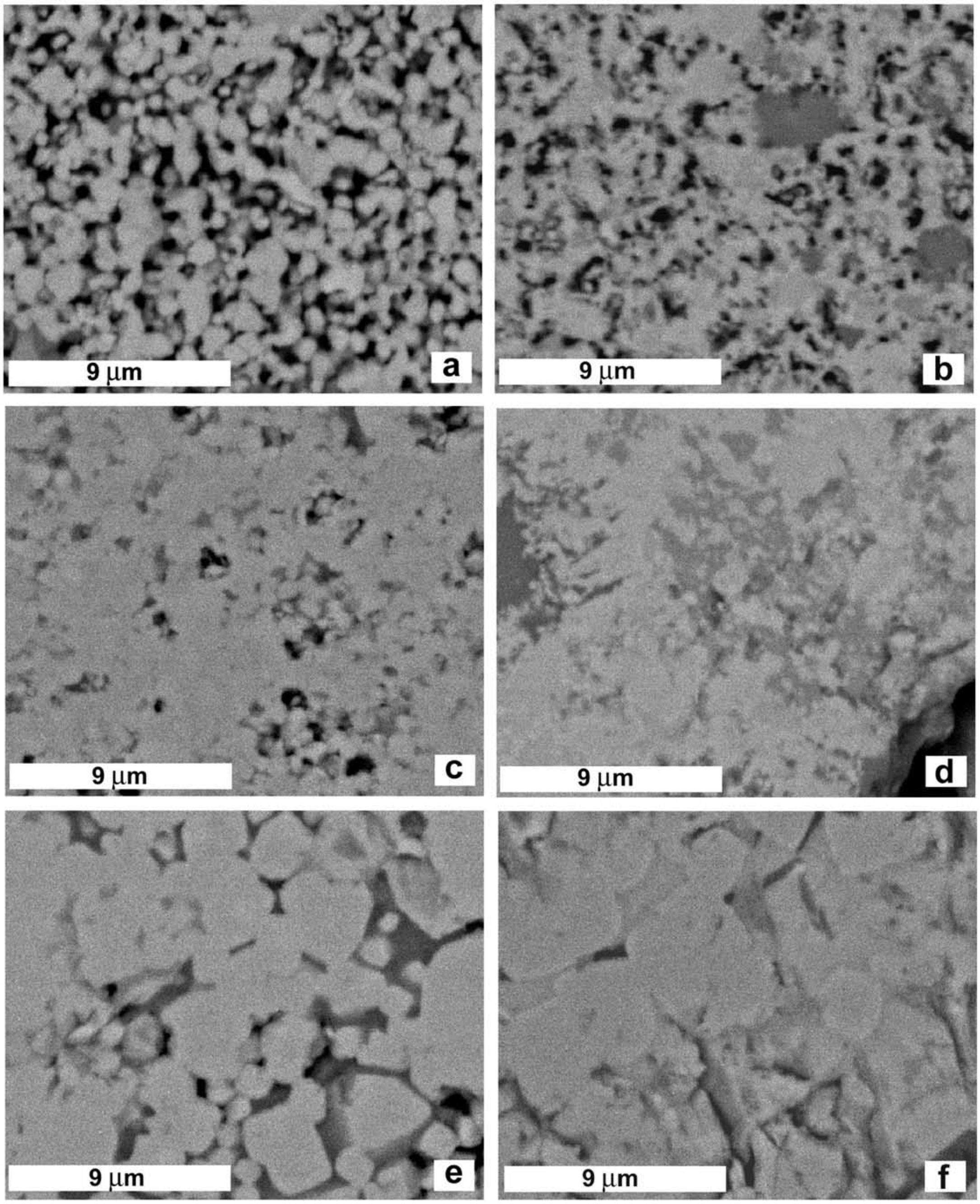

Fig. 3. Microstructures of multilayers of (a) BST-o and (b) BST-sg sintered at 1250 °C, (c) BST-o and (d) BST-sg sintered at 1300 °C, and (e) BST-o and (f) BST-sg sintered at 1350 °C.

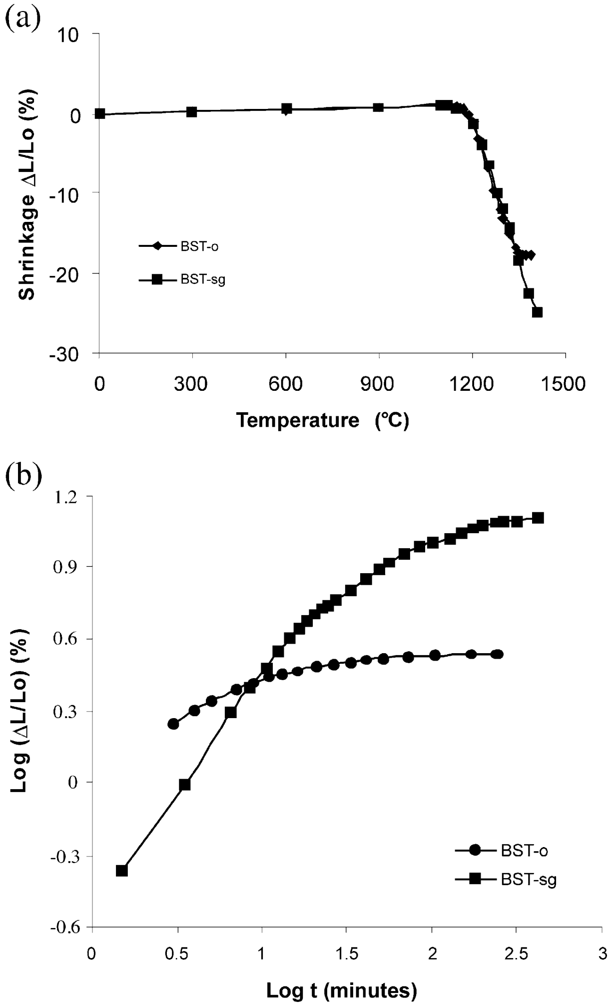

Fig. 4. Shrinkage behaviour of BST-o and BST-sg powders as a function of (a) temperature and (b) time at 1250 °C.

$$\Delta L/L_o = Kt^{1/n} \tag{1}$$

The slope of the $\log(\Delta L/L_o)$-$\log(t)$ curve is thus $1/n$. The factor n is related to the sintering mechanism, with the value of 1 proposing existence of the viscous flow dominant in sintering, 2 indicating volume diffusion and 3 standing for grain boundary diffusion.[11]

From Fig. 4(b) it can be seen that the shrinkage processes of BST-sg and BST-o powders were divided into three stages. In the first stage ($t = 0$–10 min), the n of BST-o was determined to be 2, while the n of BST-sg was 1. This means that BST-o shrinks by volume diffusion and BST-sg mainly by viscous flow, which is understandable for a microstructure containing ultra-fine particles. In the second stage (t = 15–100 min), the n of BST-o was 3 and the n of BST-sg was 2. This means that the shrinkage process of BST-o is determined by a sliding and grain boundary diffusion process, whereas the sintering of BST-sg is dominated by volume diffusion. In the third stage ($t > 100$ min), BST-sg shrinks by grain boundary diffusion (n was 3), while BST-o shows constant shrinkage. Thus, these results also indicate that tapes prepared from fine BST-sg powder do not actually require a firing temperature much higher than 1250 °C, while a longer dwell time is required for proper firing density. These results indicate that appropriate sintering of BST-sg at 1250 °C can be performed with a dwell time of 2–3 h. More detail microscopic studies are however needed to confirm the exact mechanisms.

4. Summary

Ultra-fine BST powder with particle size range from 0.05 to 0.1 μm made by the sol-gel process was suitable for making tapes by the common tape casting process. Because it is difficult to make slurry for high SSA powder, the slurry composition for BST-sg was studied. The BST-sg green tapes obtained had relatively high tensile strength and large shrinkage, and their sintering temperature was lower (1250 °C) than that of commercial BST-o (1350 °C). Isothermal dilatometric measurements showed different firing mechanisms for BST-sg and BST-o and three stages of sintering behaviour. The densification of BST-sg proceeded from viscous flow through volume diffusion to grain boundary diffusion.

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